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EQUIPMENT FOR PHASE BEHAVIOR STUDIES:
THE HYDROGEN SULPHIDE-NORMAL BUTANE SYSTEM AT 100°F

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE IN CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING

by

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EDMONTON, ALBERTA

JUNE 22, 1962

ABSTRACT

Equipment for the study of vapor-liquid equilibrium in multicomponent systems has been designed and tested. The equilibrium cell was designed to be suitable for use over a range of temperatures and pressures with systems containing hydrogen sulphide. The equipment was calibrated to 2000 lb/sq in abs and 185°F but should be suitable to pressures of 8000 lb/sq in abs and temperatures of 300°F. The design of the equilibrium cell provides for an improved method of locating the meniscus and, in conjunction with it, new methods of attaining equilibrium and obtaining samples of the phases.

Data for the pressure-composition diagram of the system n-butane-methane at 100°F were determined. A comparison with data from the literature showed agreement within 0.02 weight fraction methane. Compressibility factors for methane were obtained at several pressures at constant temperature. A comparison with data from the literature showed a maximum deviation of -0.003 in the compressibility factor.

The pressure-composition diagram of the system n-butane-

hydrogen sulphide was determined at 100°F. Compressibility factors for three compositions of this binary system were obtained at pressures below the dew point at 100°F. The experimental equilibrium ratios for n-butane and hydrogen sulphide in the binary system were compared to predicted values. They agreed at pressures lower than 100 lb/sq in abs, but differences of up to 30% occurred at higher pressures.

ACKNOWLEDGEMENTS

The author wishes to express his sincere thanks to Dr. D.B. Robinson, Head of the Department of Chemical and Petroleum Engineering, University of Alberta, for his guidance, encouragement and helpful criticism during the course of this project.

To all those friends and colleagues who have contributed in any manner to the completion of this investigation, the author offers sincere thanks. Acknowledgement is made to the Humble Oil Company for their design information. Thanks is extended to Mr. F. Butz and his staff for their co-operation in the building of the equipment. The author would also like to express his appreciation to Mr. R. Hemmings for his generous help in the assembly and calibration of the equipment. The assistance of Mr. D. Shaw regarding preparation of samples is acknowledged.

The author is indebted to the Shell Oil Company of Canada, Ltd. for the award of their fellowship and to the National Research Council of Canada and Imperial Oil Company Ltd. for their financial assistance.

TABLE OF CONTENTS

	page
List of Figures	i
List of Tables	iii
A INTRODUCTION	1
B THEORY	6
1 High Pressure Design	6
2 Phase and Volumetric Behavior	14
(a) Phase Behavior	14
(b) Volumetric Behavior	18
C MEASUREMENT OF VAPOR-LIQUID EQUILIBRIUM	20
1 Background	20
2 Cell Design	33
(a) Features of Design	33
(b) Description of Cell and Components	37
i Cell Body	37
ii Piston	45
iii Internal Valve	48
iv Gaskets	51
v Thermocouple Assembly	51

3	Auxiliary Apparatus	52
	(a) Double-acting Mercury Pump	52
	(b) Micrometer Sample Pump	52
	(c) Temperature Bath	56
	(d) Periscope Assembly	59
	(e) Other	62
	(f) Assembled Apparatus	62
4	Calibration of Apparatus	65
	(a) Temperature	65
	(b) Pressure	65
	(c) Volume	66
	(d) Chromatographic Analysis	67
D	EXPERIMENTAL TECHNIQUES	68
1	Assembly of the Cell	68
2	Preparation of Samples	71
3	Charging of the Cell	73
4	Attainment of Equilibrium	73
5	Sampling Procedure	74
6	Measurement of Volumes	76
7	Analysis	77
8	Mercury Cleaning	77

E	EXPERIMENTAL RESULTS	80
1	System Methane-n-Butane at 100°F	80
2	Compressibility Data on Methane	80
3	System n-Butane-Hydrogen Sulphide at 100°F	80
F	DISCUSSION	88
1	Experimental Results	88
2	Experimental Equipment	95
	NOMENCLATURE	98
	BIBLIOGRAPHY	100
	APPENDIX	
I	Tabulations of Experimental Results	105
II	Calibrations	112
III	Sample Calculations	119

LIST OF FIGURES

	page
1 Vapor-Liquid Equilibrium Cell Section	38
2 Cross-section of Cell Body	39
3 Sections of Cell Body	40
4 Cell Assembly	41
5 Top End Plate	43
6 Bottom End Plate	44
7 Exploded View of Window Assembly	46
8 Window Cap	47
9 Piston Detail	49
10 Internal Valve Detail	50
11 Double-Acting Pump Assembly	53
12 Pump Piston and Cylinder Detail	54
13 Double-Acting Pump in Place	55
14 Micrometer Pump Assembly	57
15 Micrometer Pump Details	58
16 Temperature Bath	60
17 Periscope Assembly	61
18 Schematic Diagram of Equipment	63
19 Assembled Equipment	64
20 Distilling Flasks	79

21	Pressure-Composition Diagram at 100°F of the System $\text{CH}_4 - \text{nC}_4\text{H}_{10}$	81
22	Pressure-Composition Diagram of $\text{H}_2\text{S} - \text{nC}_4\text{H}_{10}$ System at 100°F	82
23	Equilibrium Ratios of $\text{H}_2\text{S} - \text{nC}_4\text{H}_{10}$ System at 100°F	84
24	Diagram of H_2S Bubble Point	85
25	Compressibility Factors for $\text{nC}_4\text{H}_{10} - \text{H}_2\text{S}$ mixtures at 100°F	87
26	Pressure-Composition Diagrams at 100°F of the Systems $\text{H}_2\text{S} - \text{C}_3\text{H}_8$, $\text{H}_2\text{S} - \text{nC}_4\text{H}_{10}$, and $\text{H}_2\text{S} - \text{nC}_5\text{H}_{12}$	90
27	Equilibrium Ratios for nC_4H_{10} at 100°F	92
28	Equilibrium Ratios for H_2S at 100°F	94
29	Thermocouple Calibration	113
30	Pressure Gauge Calibration	114
31	Volumetric Calibration of Double-Acting Pump	115
32	Effect of Pressure on Cell Volume	116
33	Chromatographic Calibration for $\text{CH}_4 - \text{nC}_4\text{H}_{10}$ Mixtures	117
34	Chromatographic Calibration for $\text{H}_2\text{S} - \text{nC}_4\text{H}_{10}$ Mixtures	118

LIST OF TABLES

	page
1 Vapor-Liquid Equilibrium Data for the System n-Butane-Methane at 100°F	106
2 Methane Compressibility Factors	107
3 Vapor-Liquid Equilibrium Data for the System n-Butane-Hydrogen Sulphide at 100°F	108
4 Equilibrium Ratios for the System n-Butane- Hydrogen Sulphide at 100°F	109
5 Pressure-Volume Data for the System n-Butane- Hydrogen Sulphide at 100°F	110
6 Smoothed Compressibility Factors for the System n-Butane-Hydrogen Sulphide at 100°F	111
7 Equipment Classifications	122

A INTRODUCTION

A considerable amount of data has been accumulated over the years from the studies of numerous investigators in the field of vapor-liquid equilibrium. Nevertheless, for many systems, little or no information is available. The applicability of existing methods of predicting vapor-liquid equilibrium is subject to many restrictions; a single comprehensive theory is still to be developed. Thus, experimental programs are necessary to provide data for systems of industrial and academic interest, and to contribute to the development of an accurate theory.

In Alberta, various oil and gas reservoirs contain hydrogen sulphide and carbon dioxide in high concentrations. A study of the influence of non-hydrocarbon components, such as hydrogen sulphide, on the behavior of hydrocarbon systems is, therefore, of considerable interest. Prediction of reservoir behavior and operation of processing facilities would benefit from a better understanding of these systems. Most of the binary systems containing paraffin hydrocarbons have been investigated; however, data on the system n-butane-hydrogen

sulphide have not been reported in the literature. Consequently, this system was chosen for investigation.

The vapor pressure of hydrogen sulphide was reported by West (75) and Reamer, Sage and Lacey (48) presented data on its phase and volumetric behavior. Vapor-liquid equilibrium data for the system hydrogen sulphide-methane were published by Reamer, Sage and Lacey (49) as a sequel to their work on pure hydrogen sulphide. The data on this system were extended to lower temperatures by Kohn and Kurata (30) in 1958. Kay and Brice (27) studied the phase behavior of the system hydrogen sulphide-ethane and found azeotropic behavior. Azeotropes occurred at compositions high in ethane and existed to the critical region. Data on the system hydrogen sulphide-propane, were reported by Kay and Rambosek (29) in 1953 and again in 1961 by Brewer, Rodewald and Kurata (7) who included lower temperature data down to the solid-liquid-vapor region. This system was also shown to contain azeotropes persisting to the critical region. The azeotrope was indicated with low propane compositions, decreasing in propane content to the critical. Reamer, Sage and Lacey (53) reported no azeotrope in the system n-pentane-hydrogen sulphide. Reamer, Selleck, Sage and Lacey (54) found the system n-decane-hydrogen sulphide to be of the common binary variety, exhibiting no unusual

behavior. The phase behavior of hydrogen sulphide with carbon dioxide was investigated by Bierlien and Kay (4). They reported a tendency toward azeotrope formation but no actual azeotrope. Their data agreed well with that of Kurata and Sobocinski (31) who also extended the data to the solid-liquid-vapor region. The phase equilibria of the system hydrogen sulphide-water were presented by Selleck, Carmichael and Sage (68). Data on the ternary system hydrogen sulphide-methane-carbon dioxide were reported by Robinson and Bailey (57) for three pressures at 100°F. Data for this system over a wider range of conditions were given by Robinson, Lorenzo and Macrygeorgos (58). Systems containing hydrogen sulphide with ethanolamines were investigated by various workers, a recent example being the work of Atwood, Arnold and Kindrick (2) on the system hydrogen sulphide-water-ethanolamines.

The thermodynamic properties of n-butane are well known and have been tabulated (64). The phase behavior of n-butane with the light hydrocarbons has received considerable attention. Nederbragt (37) studied the system n-butane-methane at several temperatures and pressures. Sage et al (45,59,60) extended the data to 10,000 psia and 300°F, and included volumetric data. McKetta and Katz (33) reported a check within $\pm 1\%$ of some of

this work. Rigas, Mason and Thodos (55) presented data on the same system at 100°F which also checked well with that of Sage. Kay (26) studied the system ethane-n-butane over a range of pressures and temperatures to the critical region. Propane-n-butane phase equilibria were reported by Nysewander, Sage and Lacey (38). The system n-butane-isobutane was investigated by Sage and Lacey (63). The phase behavior of the ternary system methane-n-butane-decane was studied extensively by Reamer et al (44, 47, 50, 52). Data on the system methane-propane-n-butane at 100°F were reported by Rigas, Mason and Thodos (56). A number of binary systems containing n-butane with non-hydrocarbons have been investigated. In 1944 Reamer, Olds, Sage and Lacey (46) reported phase behavior for the system n-butane-water. This was extended in 1952 by Reamer, Sage and Lacey (51). Poettman and Katz (42) reported data on the system n-butane-carbon dioxide. This system was also studied by Olds, Reamer, Sage and Lacey (40). A study of vapor-liquid equilibria in the system n-butane-hydrogen was made by Aroyan and Katz (1). The system was shown to involve retrograde condensation of the second kind. The system n-butane-ammonia was shown to exhibit azeotropy by Kay and Fisch (28).

An interesting aspect of some of the aforementioned systems is their non-ideal phase behavior. In particular, the fact that azeotropes occur in the ethane and propane systems with hydrogen sulphide but not in the pentane system leads to speculation about the behavior of the system containing n-butane with hydrogen sulphide. This factor was another reason for the investigation of the n-butane binary system.

It was also noted that ternary and higher multicomponent systems involving acid-gases and hydrocarbons have not been investigated very extensively. Therefore, it was decided that the new apparatus to be built for studying the binary system n-butane-hydrogen sulphide would be designed for ease of operation with systems containing more than two components as well as with binary systems.

B THEORY

1 HIGH PRESSURE DESIGN

For equipment to be used at high pressures, design features are employed that are not encountered in designs for atmospheric pressure. Various techniques of design have evolved from experience and experiment. In addition, theory applicable to the problems of high pressure vessels has been developed. In general, consideration must be given to prevent leakage of system contents, to provide access and workability, and to provide for safety in operation.

Many pressure vessels are cylindrical, requiring high pressure end closures. Of course, closures may be welded or one end may be left solid; however, operating factors such as maintenance, may necessitate removal of end closures. Seals for removable end closures fall into two classes: those requiring external compression, and those using self-sealing principles. Compression seals rely on compressing a gasket so that a greater pressure is exerted on the gasket by the closure than would be encountered in the interior of the cell. Self-sealing designs enable the

internal pressure to assist in making the desired seal. The gasket is also under a greater pressure than the cell pressure in the self-sealing arrangement. Compression seals often take the form of a confined ring, although plain flat gaskets and knife-edge seals are used. Common self-sealing gaskets are those using the Bridgman (8) unsupported area principle, the delta ring, the "O" ring and the lens ring. The design of the closure also varies and may employ either type of seal. Flanged types and screwed types are often used. A variation on the screwed closure is the compression head. Bridgman-type closures and modifications are designed to provide a greater area for the hydraulic force than is allowed for the gasket. The effect is to maintain a greater pressure in the gasket than in the cell. In dealing with high pressure techniques, books by Comings (10), Perry (41) and Tongue (72) give good coverage of closure design.

For the design of cylinder walls, a theoretical approach has been used. As the pressure to be contained is increased, the thickness of the cylinder walls must be increased. As the wall thickness increases, account must be taken of the non-uniform distribution of stress in the wall. The formulas of Lamé, (the derivations of which are presented by Comings (10) and

Timoshenko (71)), are used to calculate the distribution of stresses in thick-walled cylinders.

$$\frac{\sigma_t}{P_1} = \frac{+ 1 - (P_2/P_1)k^2 + (r_2^2/r^2) (1 - P_2/P_1)}{k^2 - 1}$$

$$\frac{\sigma_r}{P_1} = \frac{- \left[(P_2/P_1)k^2 - 1 + (r_2^2/r^2) (1 - P_2/P_1) \right]}{k^2 - 1}$$

where

σ_t = stress in the tangential or hoop direction

σ_r = stress in the radial direction

P_1 = internal pressure

P_2 = external pressure

r_1 = internal radius

r_2 = external radius

r = radius at any distance from the centre

$k = r_2/r_1$

The above results are for the analytical solution of a force balance on a thick-walled cylinder under elastic conditions.

Another useful concept is the shear stress in the cross-sectional plane, σ_s which is given by

$$\sigma_s = \frac{(P_2 - P_1) r_2^2 r_1^2 / r^2}{r_2^2 - r_1^2}$$

For a cylinder with end covers, the end load must be carried by the axial stress in the cylinder. This axial or longitudinal stress, σ_a , is

$$\sigma_a = \frac{-P_2 r_2^2 + P_1 r_1^2}{r_2^2 - r_1^2}$$

It can be seen from the above equations that σ_t , σ_r , and σ_s have their greatest values at the inside surface. In most cases, the external pressure, P_2 , is negligible so that the formulas at the maximum values of stress are simplified to the following:

$$\frac{\sigma_t}{P_1} = \frac{k^2 + 1}{k^2 - 1} \quad (\text{often called the Lamé Formula})$$

$$\frac{\sigma_r}{P_1} = -1$$

$$\sigma_s = P \frac{k^2}{k^2 - 1}$$

Thus, the maximum stress is a circumferential tensile stress and occurs at the inner radius, r_1 .

In order to design a safe vessel, it has generally been considered necessary to keep the stresses below the elastic failure limit at the inner wall of the vessel. A criterion of failure must be established and combined with an equation such as the aforementioned, relating maximum stress to the geometry of the vessel. Several theories of failure have been proposed and are discussed in detail by Seely and Smith (67). The common theories are: the maximum principal stress theory, the maximum shearing stress theory, the maximum strain theory, the maximum strain energy theory, the maximum energy of distortion theory and the maximum octahedral shearing stress theory.

The maximum energy of distortion theory and the maximum octahedral shearing stress theory give the same results. The octahedral shearing stress theory enables stresses to be used in applying the energy of distortion theory instead of dealing with energy directly. This theory is sometimes known as the shear-strain-energy theory and is associated with the names of Henky and Von Mises. The energy of distortion theory states that inelastic action at any point in a body under any combination of stresses begins only when the strain energy of distortion

per unit volume absorbed at the point is equal to the strain energy of distortion absorbed per unit volume in a specimen in the tensile test. The design equation becomes

$$\frac{P_1}{\sigma_e} = \frac{k^2 - 1}{\sqrt{3} k^2}$$

This theory is regarded as the most satisfactory for a ductile metal under static load.

In the tensile test, it is often difficult to assign an exact value to the elastic limit and frequently the yield strength at a given offset is used. A safety factor can be introduced into the above equations as a multiplying factor on the design pressure. Thus, the theory of shear-strain-energy would result in the following design equation, as recommended by Manning (34)

$$k = \sqrt{\frac{y}{\sigma_y - s P \sqrt{3}}}$$

σ_y = yield stress

s = safety factor

The Autoclave Engineering Corporation (18, 19) uses the

Lamé formula combined with an allowable stress set forth in the ASME Code. The Code presents a formula for use to 3000 psi. Using the Lamé formula with the allowable stress amounts to adding a safety factor to the design yield stress in the maximum principal stress theory. Lindroos (32) used this theory in his low temperature design. Practice varies in the method of attributing safety factors, with the result that a larger safety factor is used for the maximum stress theory than for the recommended criterion of elastic failure, the shear-strain-energy theory.

A pressure in excess of the overstrain pressure is usually required to burst a thick-walled cylinder. Sometimes it is assumed that the ultimate tensile stress may be substituted for the yield stress in the design equation. When the yield stress is less than the ultimate tensile stress it is sometimes postulated that

$$P_b = \left[2 - \left(\frac{\sigma_y}{\sigma_v} \right) \right] \frac{2\sigma_y}{\sqrt{3}} \ln k$$

where

P_b = bursting pressure

σ_v = ultimate tensile strength

which reduces to

$$P_b = \frac{2\sigma_y}{\sqrt{3}} \ln k \text{ when } \sigma_y = \sigma_v$$

The formula above is an approximation and does not apply when large wall thicknesses are involved. A discussion of very high pressure considerations is given in Hamann (22).

The foregoing discussion has been concerned with stresses in uniform cylinders under static loading conditions. Temperature gradients, openings in the wall, points of sharp curvature, and fatigue often enter into the design of a vessel, each resulting in stress distributions different from that in the simple cylinder. Comings (10) presents an analytical treatment for the effect of a temperature gradient. Faupe1 (17) has presented an analysis on the effect of side holes in heavy walled cylindrical vessels. Fatigue and creep effects are dealt with qualitatively by Manning (34). Most design methods appear to depend on a safety factor to account for discontinuities, since theory has not been developed for most highly concentrated stresses of a localized nature.

2 PHASE AND VOLUMETRIC BEHAVIOR

(a) Phase Behavior

A phase may be defined as a homogeneous, mechanically separable portion of a system. Assuming that the only limiting variables are temperature, pressure, and composition, Gibbs' Phase Rule may be applied to any system in heterogeneous equilibrium. The Phase Rule relates the number of degrees of freedom or variance, F , the number of components, C , and the number of phases, N , as follows:

$$F = C - N + 2$$

Thus, for a two component system,

$$F = 4 - N$$

If two phases are present, two intensive variables such as temperature and pressure must be specified to define the system.

In the calculation of the compositions of the phases, simplifying assumptions are often made to give approximate values, or to help explain the deviations from ideal cases. Raoult's Law and Dalton's Law are two idealized relationships used to describe the liquid and gas phases respectively. For the prediction of vapor-liquid equilibria they may be combined to give:

$$y_i P = x_i P_{vi}$$

y_i = mole fraction in the vapor

x_i = mole fraction in the liquid

P_{vi} = vapor pressure of component i at the temperature of the system

P = total pressure of the system

Raoult's Law assumes that the molecules in the liquid behave similarly and that they mix without complicating side effects such as molecular association and chemical combination. Dalton's Law assumes the ideal gas law applies to the vapor phase.

Another concept that is useful is that of the ideal solution. The assumptions made are that the partial volumes are additive and the internal energies are additive, i.e. no heat of solution. For an ideal solution, the fugacity of each component in a phase is equal to the fugacity of that component in the pure state in the same kind of phase at the same temperature and total pressure times its mole fraction. When phases are in equilibrium, the fugacity of a component must be the same in all phases present. Thus, for an ideal solution

$$\frac{y_i}{x_i} = \frac{f_{i1}}{f_{ig}}$$

f_{il} = fugacity of pure liquid component, i ,
at the temperature and pressure of the
mixture

f_{ig} = fugacity of pure gaseous component, i ,
at the temperature and pressure of the
mixture.

It will be noted that for an ideal solution, fugacities have replaced pressures in Raoult's and Dalton's relationship.

Deviations from the ideal laws may be expected because of inequalities in the volumes of the molecules or disparities in the molecular forces. The first of these becomes important only when molecules differ greatly in size and leads to negative deviations from Raoult's Law. Both positive and negative deviations from Raoult's Law occur when molecular forces are significant. Examples of forces that cause deviations are dipole moments and London dispersion forces.

A common type of non-ideal behavior is that encountered when azeotropes occur. It has been found that azeotropes are likely to occur in systems which have component critical temperatures that are close together and critical pressures that are far apart.

It is convenient to simplify the ideal solution equation to the form

$$\frac{y_i}{x_i} = K \quad \text{where} \quad K = \frac{f_{il}}{f_{ig}}$$

The values of the equilibrium ratio, K , calculated from the fugacities are termed ideal solution K 's. Experimentally determined K values are found to be a function of pressure, temperature, and the nature and amount of all components present, that is, ideal solution laws are not necessarily obeyed. The use of the equilibrium ratio is convenient and is a common method of expressing experimental results.

It was found that, at constant temperature and for increasing pressure, the K values of each component in a hydrocarbon system of fixed composition converged toward a value of unity at some high pressure. This pressure was termed the convergence pressure and for a binary system has been defined as the critical pressure of a mixture of that composition which has a critical temperature equal to the temperature of the system being considered. Methods have been developed for predicting convergence pressures and charts have been presented (21,77) for obtaining the equilibrium ratio when the convergence pressure is known.

The use of the convergence pressure concept for all mixtures is not recommended as it was developed for hydrocarbons. The use of activity coefficients and normal boiling points in prediction methods is seen as a more fruitful approach to an overall theory for the prediction of vapor-liquid equilibrium

(b) Volumetric Behavior

Equations of state have been used extensively to describe behavior in the gas phase. For engineering purposes, the ideal gas law has been modified by inclusion of a correction factor termed the compressibility factor, Z .

$$PV = ZnRT$$

Experimental values of the compressibility factor may be plotted as a function of pressure with temperature as a parameter, or they may be presented in the form of generalized charts. For the latter, the theorem states that two substances should have similar properties at corresponding conditions with reference to some basic property such as the critical temperature and pressure. Thus, the compressibility factor is plotted as a function of reduced temperature and reduced pressure. Mixtures are treated by employing pseudocritical temperatures and pseudocritical pressures.

The equation of state of a gas at moderate pressures may be expanded in power series form

$$PV = RT + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \dots$$

This equation is known as the virial equation of state and the

coefficients B , C , ... are called virial coefficients. They are dependent only on temperature in a single component system, but for mixtures, they are functions of composition as well as temperature. Accurate values of second virial coefficients, B , and higher coefficients, C , are available for few systems as special low-pressure equipment is necessary to obtain the experimental values.

C MEASUREMENT OF VAPOR - LIQUID EQUILIBRIUM

1 BACKGROUND

A survey was made of the equipment of other investigators to obtain a general picture of the different methods and techniques which can be used in the study of phase behavior.

The types of equipment used could be classified as follows: static, dew and bubble point recirculation, dynamic flow or equilibrium still. Other variables in designs included methods of attaining equilibrium, pressure and temperature ranges employed, provisions for windows, and methods of obtaining compositions of the phases. Most of the investigators employed static cells, although the use of the dew and bubble point method was common for the study of binary systems. A great deal of work has been done using equilibrium stills near atmospheric pressure, but their use at higher pressures is not often attempted. Some equipment designs enable volumetric as well as phase data to be obtained.

(a) Static Cells, Variable Volume

Sage, Lacey and co-workers (61,62,65) have developed

versatile equipment to obtain combined vapor-liquid equilibria and volumetric data. Their basic equipment design has not been changed although various modifications have been made over the years. They employed a spiral agitator, magnetically driven. Sample ports were provided for the liquid and for the gas, the level of the liquid or mercury being determined with an electric indicator calibrated for height. A volume compensating device was designed to maintain accurate volumes. A pressure balance was used to measure the pressures to 10,000 psi and a platinum resistance thermometer to measure the temperature from 30 to 460°F. An oil bath surrounding the cell gave close control of the temperature.

The equipment of Katz and Hachmuth (23) was also a variable volume cell using mercury as the confining liquid. An electric motor was used to drive a bladed agitator. Samples were taken from the gas and from the liquid, the amount of charge being calculated to give enough liquid to cover the liquid sample line. The maximum working volume was one litre. Standing and Katz (70) made modifications to this type of cell design. An electrical level indicator was inserted and equilibrium achieved by rocking the cell instead of using a stirrer.

Webber (73) also used a rocking device on his cell.

The cell was made from double extra heavy steel pipe with the end closures welded to the body. The one litre cell without windows was rated to 8000 psi. Samples of the gas were taken from the top of the cell and then the gas was displaced keeping the pressure constant. Then a liquid sample could be taken from the top of the cell. However, with a "blind" cell an exact knowledge of the location of the liquid interface would be difficult to obtain, with the result that errors in sampling were more likely to occur.

In the cell described by Burch (9), an internal ball-valve was closed prior to sampling. As a result, the liquid was isolated from the gas and the chance of sample contamination was reduced. A solenoid-actuated magnetic stirrer was used to speed equilibrium attainment. The author does not make clear how the liquid level was adjusted so that an exact separation of liquid and gas was achieved by the closure of the internal valve.

McKetta and Katz (33) in their study of the system methane-n-butane-water used three sampling ports, two liquid phases being obtained. To ensure the location of the interfaces, they used a windowed cell. As in (23) above, a stirring motor was mounted inside the cell.

Katz and co-workers (1, 14, 25) and Robinson et al (57, 58) have used successfully a windowed cell consisting of a liquid level sight gauge. With this type of equipment, the gauge is generally mounted in a temperature bath which permits visual observation of the gauge contents. Both air and liquid baths may be used to control temperature. Provision is made for rocking the cells on trunnions and the volume of the contents is controlled by addition or removal of mercury. The gas phase may be sampled isobarically from the top of the cell. If a liquid sample line is not provided, the liquid sample may be obtained from the top of the cell after isobaric displacement of the gas.

A rather sophisticated window design was used by Eilerts (15,16) and by Dean and Poettman (12) in their windowed cells, which were designed to measure phase volumes of condensate systems. Volumes were obtained by measuring the angle of tilt to the cell when each interface was visible in the window which was located near the axis of rotation. The windows consisted of a double window with a water-white mineral oil seal between the windows. The pressure on this oil was maintained equal to the internal cell pressure. The internal window was supported on an "O" ring while the external window was sealed glass to metal utilizing the Bridgman (8) design.

In addition Dean and Poettman (12) used a rocking windowed cell of a different design for sampling multicomponent mixtures. It consisted of three sections, one for the liquid and one for the gas, joined by a small bore section containing the windows. A liquid sample line came through the bottom closure, while the gas was sampled at the base of the gas section. The cell volume was approximately 2700 cu cm. A floating piston was employed in the top section to vary the effective volume available for the gas. Mercury was used to vary the volume of the bottom section of the cell. At temperatures from 0 to 400°F, the cell could be used to 10,000 psi. A separate cell, lined with electrical contact, was used to measure the volume of the mercury on top of the piston, while an oil pump was used to measure the volume of mercury in the section below the piston. A piston cell was employed by Sloan (69) in his studies of condensate behavior. The location of the piston was determined by attaching a gauge rod to the piston, with the rod passing through the gland on the top of the cell. As with Dean's cell, a liquid and a gas section were used with windows at a reduced-bore central portion. Equilibrium was attained using a stirrer driven by an electric motor mounted inside the cell. The motor was located in the gas section below the limit of the piston stroke. The

liquid sample line was located at the level of the windows while the gas sample line was in the wall at the lower limit of the piston stroke.

Two other designs utilizing pistons were encountered. De Priester (13) used a very simple cell consisting of a single cylinder bore which accommodated a floating piston. The hydrocarbons to be studied were contained on one side of the piston while the pressuring fluid was contained on the other side. The cell could be rocked to attain equilibrium. Vapor was sampled with the cell upright and liquid was sampled when the cell was inverted. Precautions must be taken to avoid contamination of the samples. The cell of Rigas, Mason and Thodos(55) appeared more complicated than the one of De Priester and was designed for removal of very small samples. A magnetic stirrer was used to speed the attainment of equilibrium. The stirring rod and blades were confined within an internal collar that ran the length of the cell, but with contact ports to the piston section. The piston, thus, was of a donut shape, the interior running against the stirrer collar and the exterior running against the cell wall. As in the De Priester design, the mercury and the hydrocarbon samples were separated by the piston, the mercury being on top. Neither cell could be used for obtaining liquid and

gas volumes.

A rather unique windowed cell was that reported by Wells and Roof (74). The entire working section of 125 cu cm was visible through the use of thick-walled pyrex tubing as the core of the cell. Pressure was applied axially to the tubing on the closed end, (which was also sealed from the cell interior) equal to the pressure in the interior of the cell. Thus, pressure was applied to the outside of the capillary tubing by both the cell pressure acting on the walls and an equal pressure acting on the one sealed end. The open bottom end of the tubing was made to bear against the cell body, an "O" ring making the seal. A periscope containing its own light source was run up and down the bore of the glass tubing to observe the cell interior. The cell was designed to operate to pressures of 8000 psi and temperatures of 300°F. A gas sampling port was installed in the outer wall near the top of the cell interior.

(b) Static Cells, Isochoric

A spherical pressure vessel for isochoric measurements has been described by Sage and Reamer (65) and by Selleck, Carmichael and Sage (68). The vessel was mounted in a temperature bath for accurate temperature control. As in all isochoric cells,

the pressure was measured as a function of temperature. To maintain a constant volume a compensating diaphragm assembly was used to transmit the pressure to a pressure balance. Specific volume measurements were obtained as a result of weighing the amount of sample charged. Equilibrium was hastened by the action of an agitator connected by a shaft through the cell wall to the motor. Provision was made for the withdrawal of small samples of gas and liquid.

A two-section cell with included sampling tubes was used by Boomer, Johnson and Argue (5) for pressures to 370 atm. The equipment could be rotated through 90° so that the liquid would flow from one section to the other via the liquid sampling tube. An electrical indicator was used to ensure that only liquid was in the liquid sample tube. For mixing near critical conditions, a plunger with adequate clearance for fluid leakage was inserted in the liquid sampler. The cell and sample tubes were mounted in a bath for temperature control.

In their study of the nitrogen-ammonia system to 3,750 atm, Lindroos and Dodge (32) used a constant-volume cell of 200 cu cm capacity. A solenoid-actuated stirrer with a reciprocating motion was used to speed equilibrium attainment. An intensifier in conjunction with a liquid-piston pump was used to build the

pressure to the desired level. Liquid and gas sampling ports were provided. The pressure before and after sampling was measured with a manganin resistance gauge to determine the pressure drop during sampling.

Isochoric equipment has found use in the study of vapor-liquid equilibrium at low temperatures. The use of a confining liquid which might freeze is thereby avoided. Brandt and Stroud (6) have used a windowed cell to 800 psi and -320°F . A stirring rod was incorporated in the cell to aid in reaching equilibrium. The cell was cooled with liquid nitrogen for temperature control. After the cell was cooled the sample was introduced until a visual observation indicated the desired amount of liquid to be present. After sufficient stirring, samples of the liquid and gas were taken.

(c) Dew and Bubble Point Equipment

Kay and Rambosek (29) have used a glass capillary for observing dew and bubble points and determining volumetric properties of the system hydrogen sulphide-propane. Thick-walled glass capillary tubes were also used by Gore, Davis and Kurata (20) and Nysewander, Sage and Lacey (38). A quartz tube was used by Cummings, Stone and Volante (11). The sample to be studied was confined in the capillary tube over mercury,

or a convenient fluid. A displacement pump was used to control the volume of the sample. Volumetric determinations made by measuring the location of the interfaces in the tube. A steel ball was placed inside the capillary and moved up and down magnetically to stir the sample. Temperature was controlled by an ebullient bath or a circulating fluid. A wide range of temperatures has been employed with this type of equipment. Kay and Rambosek used temperatures to 220°F with pressures to 1200 psi. Gore, Davis and Kurata also used pressures to 1200 psi and temperatures down to -200°F.

(d) Recirculation Apparatus

Apparatus, wherein the vapor is removed from the cell and recirculated to bubble through the liquid, was used by Aroyan and Katz (1) and Price and Kobayashi (43) for their studies of low temperature vapor-liquid equilibria. Price used a Jerguson gauge immersed in Dewar flask and recirculated the vapor using a magnetic pump. Aroyan also used a magnetic pump that withdrew vapor from a pressure control cylinder. Provision was made for sampling both phases. The use of the compression cell enabled the samples to be taken isobarically.

(e) Dynamic Flow Equipment

White and Brown (76) have described their equipment which incorporates the dynamic flow method of determining vapor-liquid equilibrium. This method was chosen because of its suitability for work at high temperatures, the sample contact time in the cell being low. The cell was immersed in a molten salt bath which could be heated to 1000°F. At these temperatures, the design took into account the creep properties of the metal used. The liquid level in the cell was controlled through the use of a capacitance indicator. Liquid and vapor samples could be obtained and in addition, separators were included at the outlet of the gas stream. Michels (35) also used a dynamic system in his high pressure studies. Care was taken to ensure equilibrium by passing the sample through a sintered aluminum block so that very small bubbles passed through the liquid. A mercury intensifier was used to keep the charge at a constant pressure. The vapor and liquid were sampled after equilibrium was established. A large charge sample was used to maintain a bleed rate of 20 mls per min.

(f) Equilibrium Stills

The operation of an equilibrium still can be compared to that of a distillation tower on total reflux. Heat applied

to the liquid causes vaporization, the vapors subsequently being condensed and returned to the liquid. Scheeline and Gilliland (66) have used a still made from gauge-glass tubing to 600 psi. Barr-David and Dodge (3) described a steel high pressure equilibrium still capable of operation to 3200 psi. The vapor was sampled as a liquid from the condenser while the liquid was sampled from the base of the still itself. Heat input and output were balanced so that an equilibrium temperature would prevail.

(g) Summary

The foregoing outline serves to illustrate the variety of equipment that has been used for the study of vapor-liquid equilibrium. The use of any particular type may be justified if the desired results are obtained, some being better suited to particular experiments. Static variable volume cells are suited to multicomponent system studies as samples may be taken isobarically. If volumes are desired, auxiliary apparatus and modifications to the cell are required. Windows in cells aid in observing the location of interfaces, the number of phases present, dew and bubble points, and critical opalescence. The cell designed to include windows is, however, more complicated and subject to the pressure restrictions of the transparent

material used. Static variable volume cells are generally limited to an intermediate range of temperature operation. Achieving equilibrium in static cells has presented some problems. Agitators do not always give the desired results in a short enough time and a method of actuating them results in design complications. Rocking cells give very good contact between phases but sample line connections, liquid hold-up, and the design of the temperature control bath must be taken into account. Advantages in manipulation of the sample sometimes offset the design and operation problems presented by the use of pistons. Constant volume cells and dew and bubble point cells are good for lower temperatures, but sampling is difficult. The dew and bubble point equipment is restricted to binary systems. Recirculation of the vapor gives excellent mixing. However, a good recirculation pump is required and temperature and pressure control requires a more elaborate technique. Dynamic flow also gives good mixing and approximates field conditions. A large sample is required and only one set of points may be obtained for each charge. An advantage of the equilibrium still is the relatively small influence of impurities upon the results. Shortcomings arise in the attainment of equilibrium, from entrainment in the samples, and in the need for large samples. Tempera-

ture control is also an important consideration. A listing of some classifications of the various cells mentioned in this section appears in Appendix III, Table 7.

2 CELL DESIGN

(a) Features of Cell Design

A cell was required to obtain vapor-liquid equilibria of multicomponent systems containing hydrogen sulphide. In addition, measurement of volumes was desirable to permit determination of other thermodynamic properties. The final cell design evolved from consideration of the equipment, procedures and results of other workers, as well as new ideas.

A feature which applies to any experimental equipment is that of ease of operation. Variables should be relatively simple to measure and control. The variables to be measured were pressure, temperature, phase compositions and volume at equilibrium conditions. A variable volume type cell was chosen so that the temperature could be controlled to a set value and the volume and corresponding pressure varied for a given overall composition. Mercury appeared to be suitable as a confining fluid. A cylindrical shape was chosen for the cell because design criteria are relatively better known and fabrication

is convenient.

Attention was given to the choice of a working volume for the cell. A greater range of points could be obtained with one charge if a large sample volume were available. A large volume would thus reduce the number of sample mixtures charged to the cell, and the time required to obtain a given amount of data. The time gained by eliminating charges due to lack of sample is offset by a longer period required to establish equilibrium in the larger sample. Errors in measuring volumes are reduced, especially at higher pressures, when the initial low-pressure charge is greater. However, more work is required to prepare a large initial charge than to prepare a small initial charge. Another consideration regarding volumes is the relative amounts of liquid and gas present at equilibrium. Near the dew point, the amount of liquid is small. A reduction in cross-sectional area of the cell is one method of working with smaller volumes of liquid. This method was chosen for the cell. A total volume of about 600 cu cm was chosen, the working volume to varied as necessary for the measurement being made.

In a variable volume cell, if the liquid is to be sampled, a method must be available for locating the interface

between the gas and liquid, and the interface between the liquid and mercury. Electrical probes and direct observation through windows have been used. The use of windows offers advantages for phase behavior studies that are not found with other methods, so windows were included in the cell design. Visual observation offers an opportunity to obtain dew points and to observe effects such as critical opalescence. Man's curiosity sometimes plays a part in his wanting to see visually rather than "see" through instruments. A small "bulls-eye" type of window was chosen as the most suitable for high pressures.

It was thought convenient to have the sampling port visible at the window and to locate the port at a constriction in the cell such that runs involving small amounts of liquid could be sampled. A small sample for analysis was desirable from the view-point of minimum disturbance of equilibrium, relatively constant overall composition, and greater use from a single charge. Gas-liquid partition chromatography presented a convenient method of analysis requiring only small samples. To control sampling amounts, a micrometer type displacement pump was adopted. It was deemed advisable to have a relatively short sample line, eliminating the use of a rocking cell with coils in the sample line.

To enable a cylindrical window to be used in conjunction with a reduced bore section, a floating piston was installed in the top section of the cell. The piston was to be actuated by a double-acting pump which provided a method of keeping the volume in the cell constant while raising and lowering the piston. Mercury from one cylinder of the pump was added to the top of the cell, lowering the piston. The interface could be lowered at the same time by withdrawing the same amount of mercury from the bottom section of the cell into the other cylinder of the pump.

With a device being available to transfer the interface location in the cell without disturbing equilibrium conditions, it was found that a section should be provided below the reduced bore portion of the cell. This section could then contain the liquid so that the gas could be lowered to the window and sampling line. Only one sample line was then required. As a result, the cell was designed to contain three sections, a gas section with a piston, a restriction with a window assembly, and a liquid section having less capacity than the gas section.

The double-acting pump and piston arrangement was utilized in the development of a method of attaining equilibrium

that eliminated the need for a rocking device or for mechanical or magnetic stirrers. A type of nozzle could be used to spray the fluids from the liquid section into the gas and bring about intimate contact of the phases. By raising the interface with the double-acting pump, the volume could be kept constant, equilibrium being established when the pressure stabilized.

The design was restricted to a maximum temperature of 300°F by the decomposition temperature of hydrogen sulphide. The freezing point of mercury determines the minimum operating temperature. Pressures were limited to 8000 psi maximum because the stainless steel chosen to resist attack by hydrogen sulphide has undesirable characteristics at greater pressures. The use of glass also presents limitations to operating pressures.

(b) Description of Cell and Components

(i) Cell Body The cell assembly is shown in Figure 1. For simplicity bolts, gaskets and pipe connections are not shown. The cell body specifications follow in Figures 2 and 3. Figure 4 shows the unmounted cell. Type 316 stainless steel was used throughout the cell. The bolts used were Allen-head high tensile steel with fine threads. Fittings for the sample outlet and the top and bottom plates were made for one-eighth inch

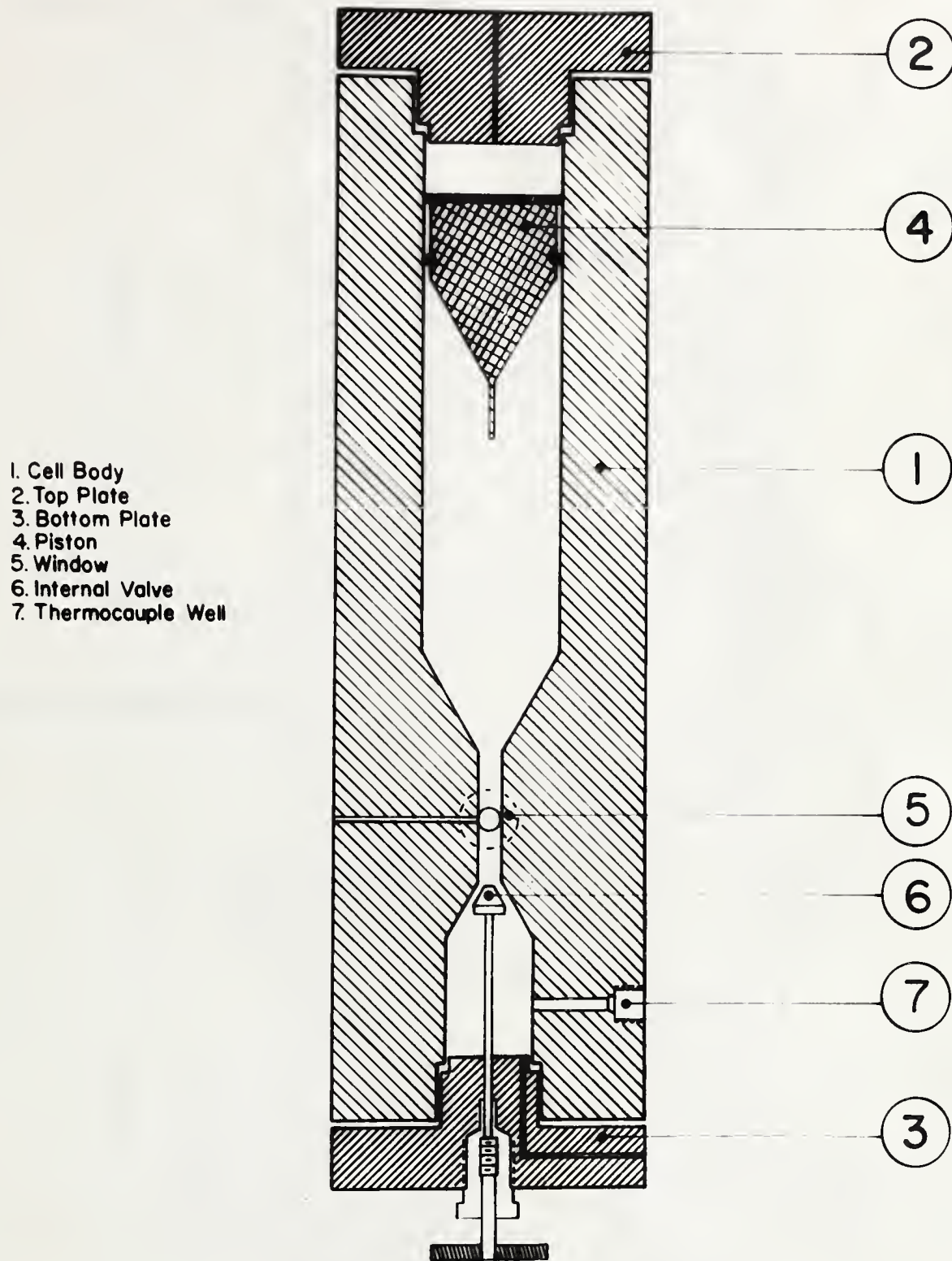
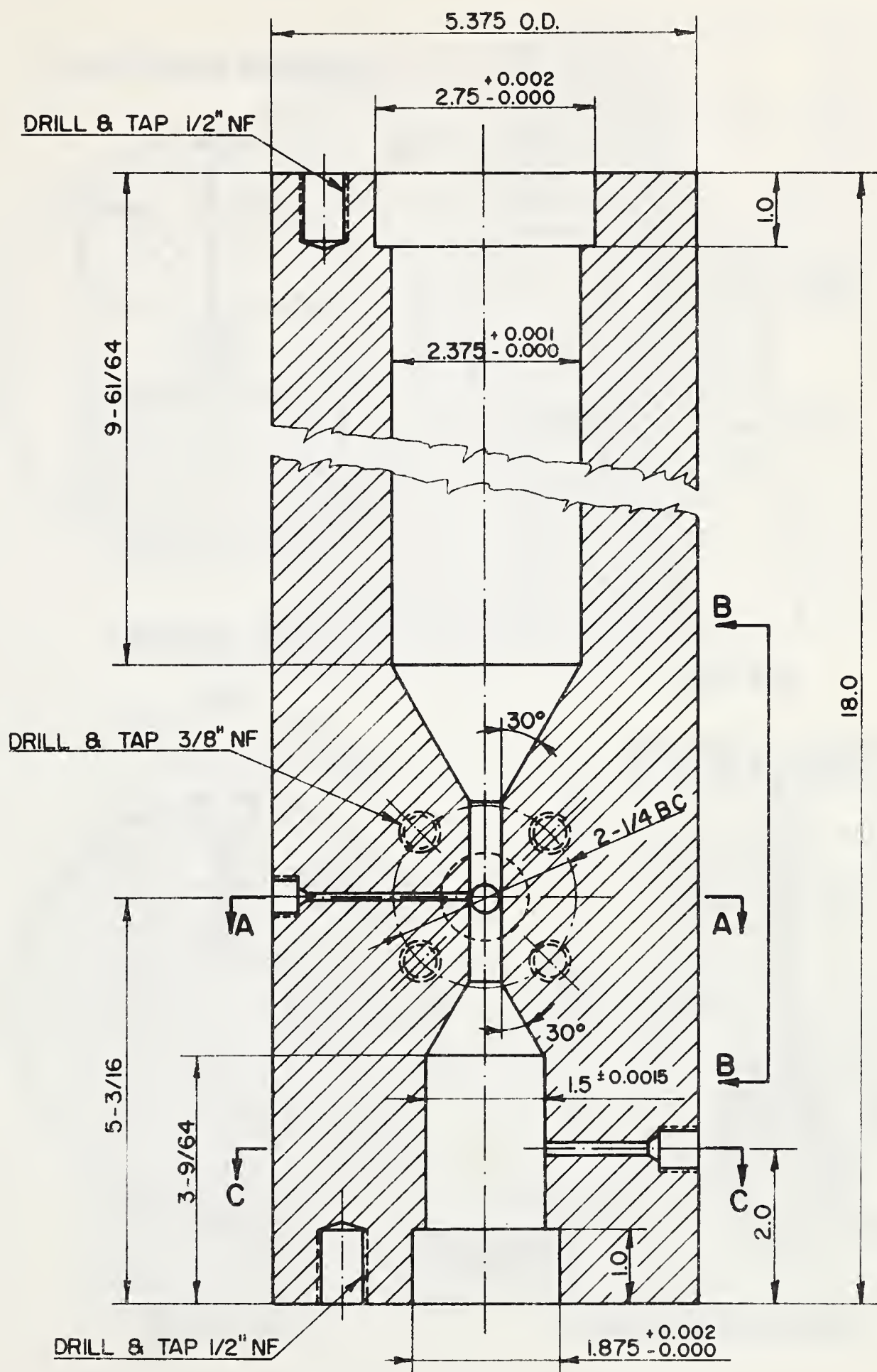
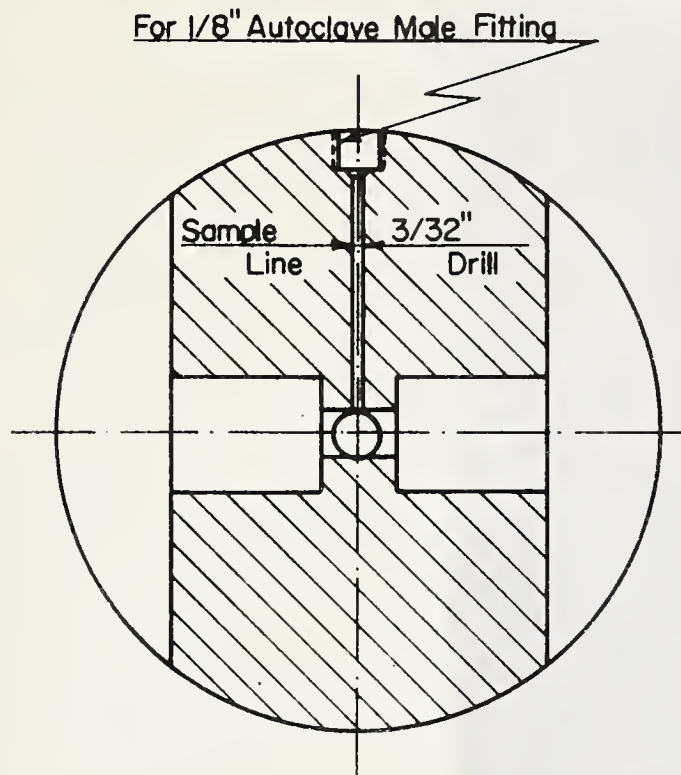


FIG. I. VAPOR-LIQUID EQUILIBRIUM CELL SECTION

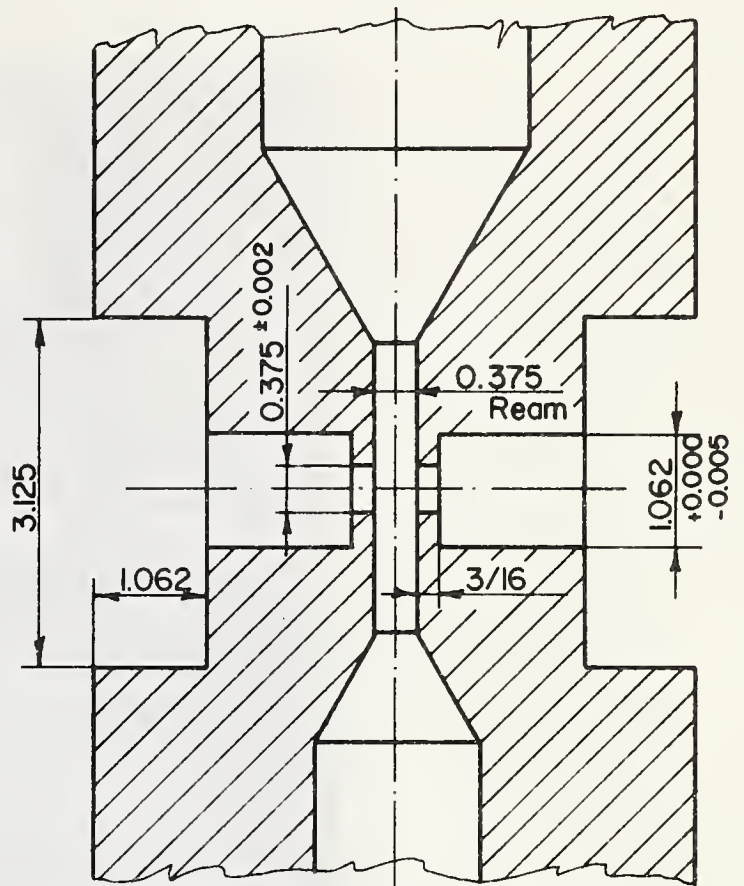


NOTES: 1. Allen Head Bolts to be used, 2. Material - 316 SS, 3. Scale - 1" = 2"

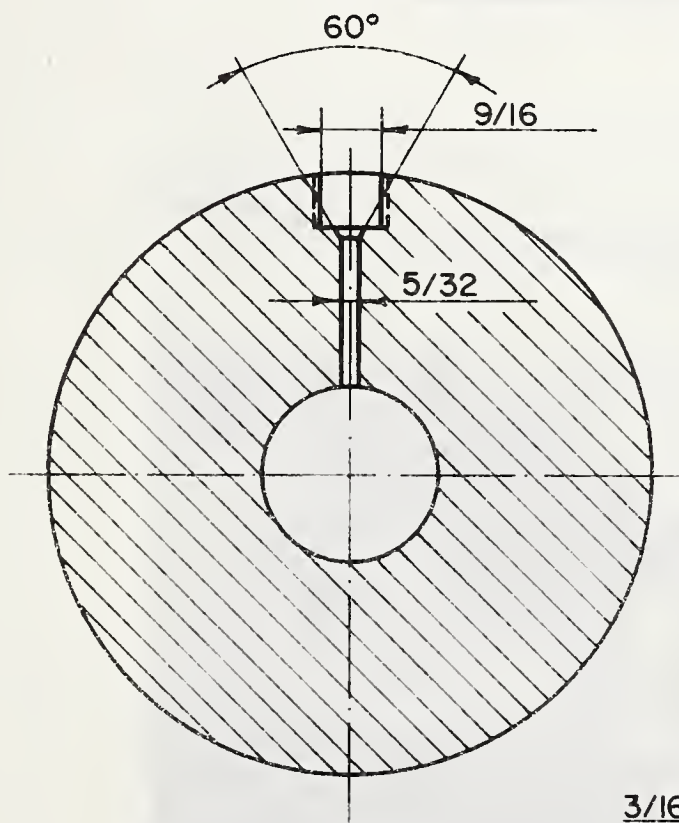
FIG. 2. CROSS-SECTION OF CELL BODY



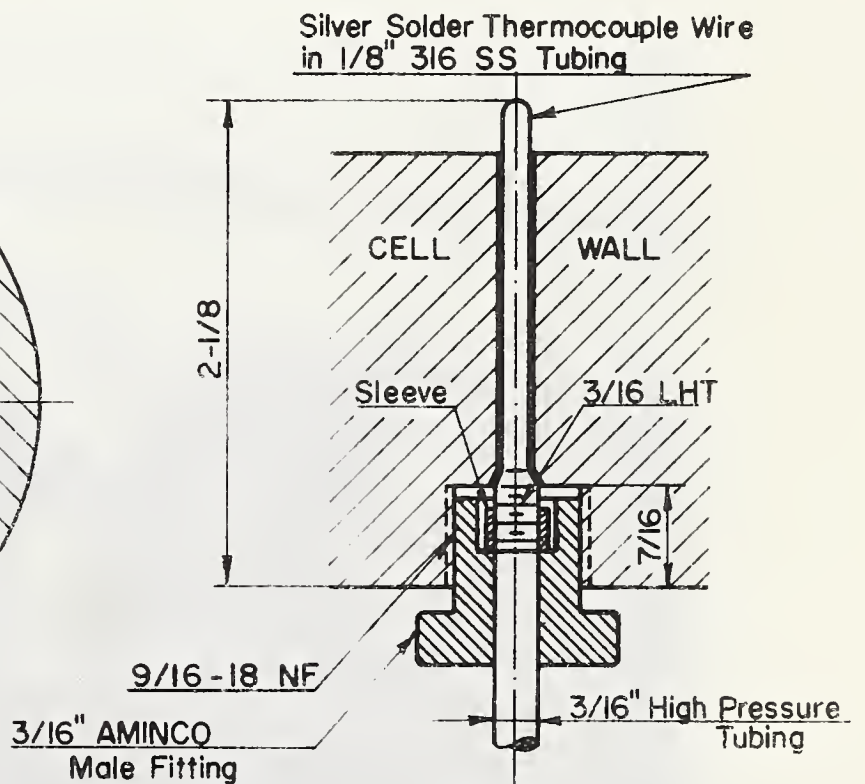
SECTION A-A



VIEW B-B



SECTION C-C



THERMOCOUPLE DETAIL - 7

FIG. 3. SECTIONS OF CELL BODY

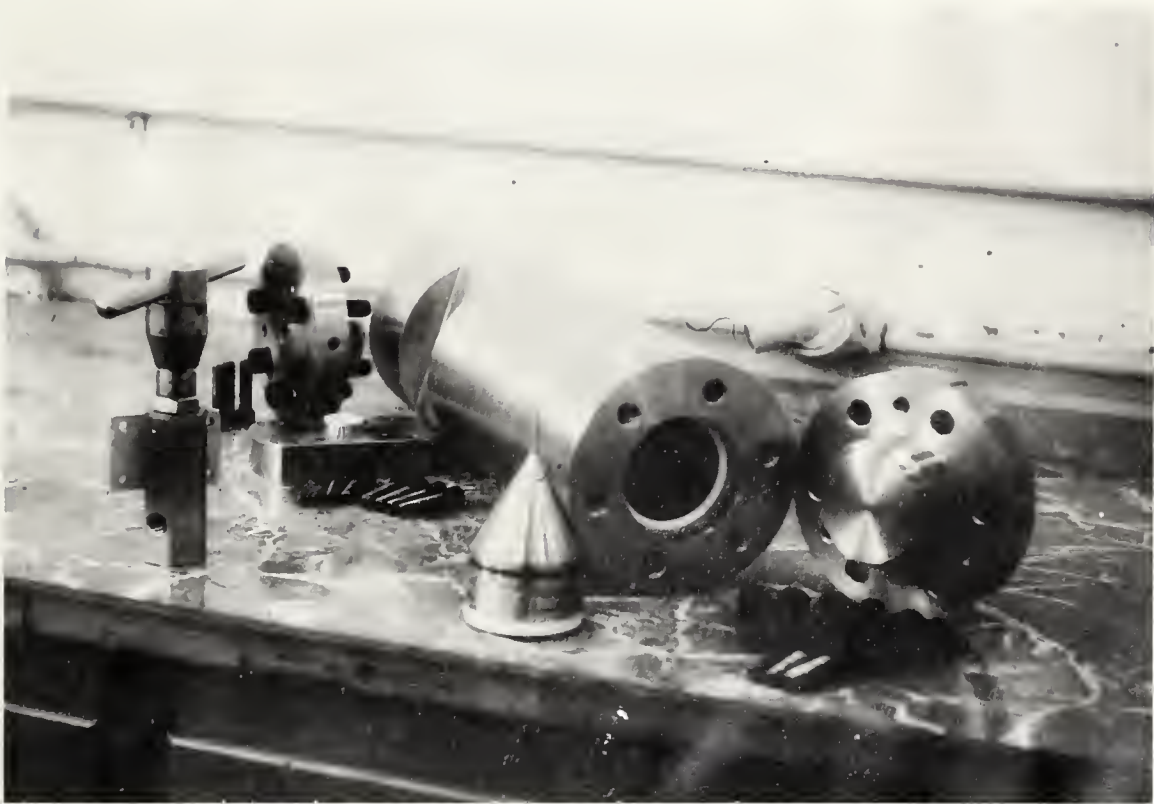
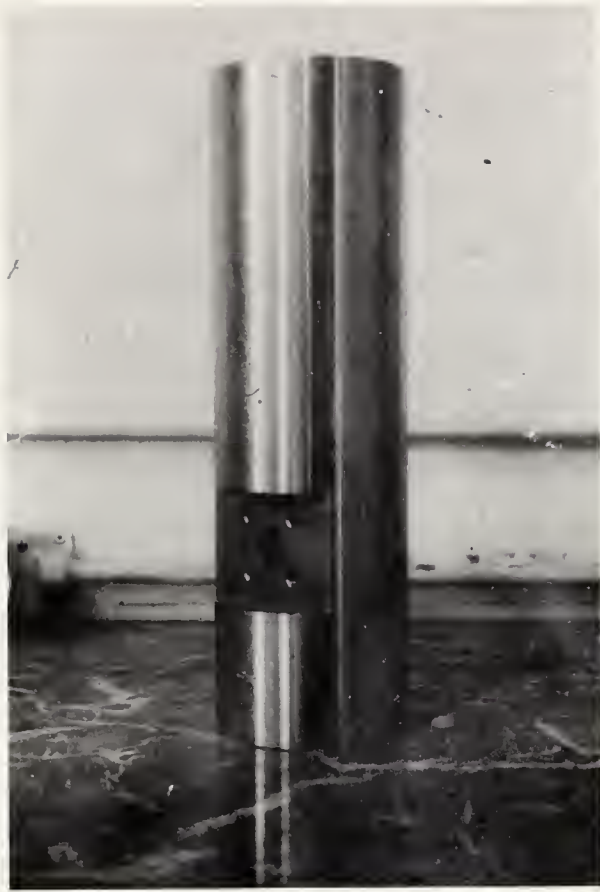


Fig. 4 CELL ASSEMBLY

Autoclave male Ermeto fittings. Calculations for the cell wall thickness are given in Appendix III. The top bore section has a safety factor of 2.3 calculated according to the Von Mises criterion for elastic yield. The central bore and bottom sections have a greater wall thickness. The window openings, sample line and thermocouple openings were put in the sections with thicker walls to reduce the effect of local stress concentration that they develop. Providing thicker wall sections for openings is general practice. The tolerances on the bore of the top section were close because of the piston requirement. Sixty degree cones were provided to lead into the central bore section from the gas and liquid sections. The cone in the gas section permitted liquid drainage.

The design of the end plates was such that they fitted a recess in the cell wall. Thus the gasket seal was made at a point lower than the region adjacent to the bolt holes. The end plates, shown in Figures 5 and 6, were made one inch thick where the bolt holes were drilled and thicker in the central core. The plate thickness at the bolt holes exceeded the ASME code specifications. For the removal of the end plates in cases of a tight fit, three bolt holes were drilled and tapped. The inserted bolts dislodged the plate.

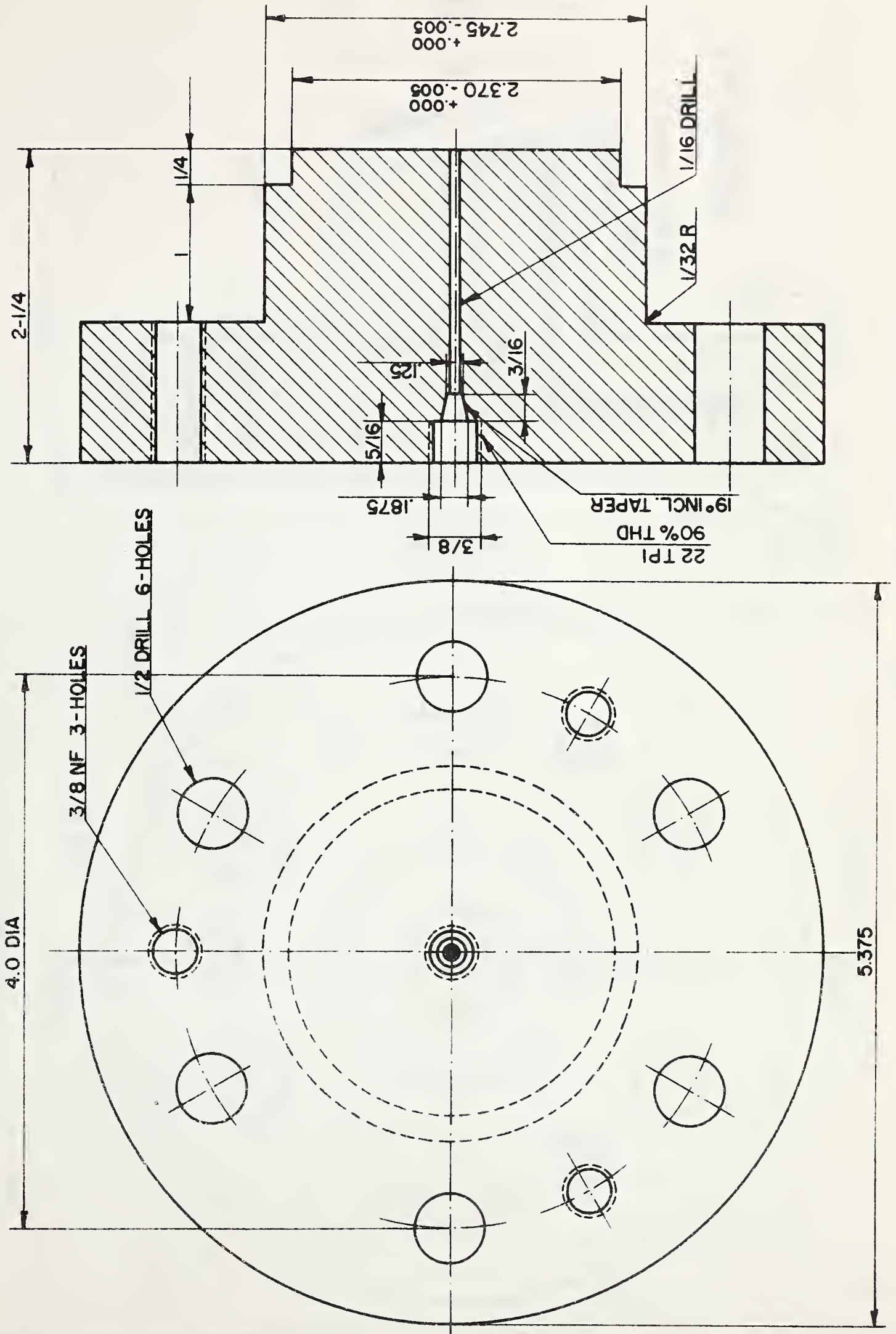


FIG. 5. TOP END PLATE

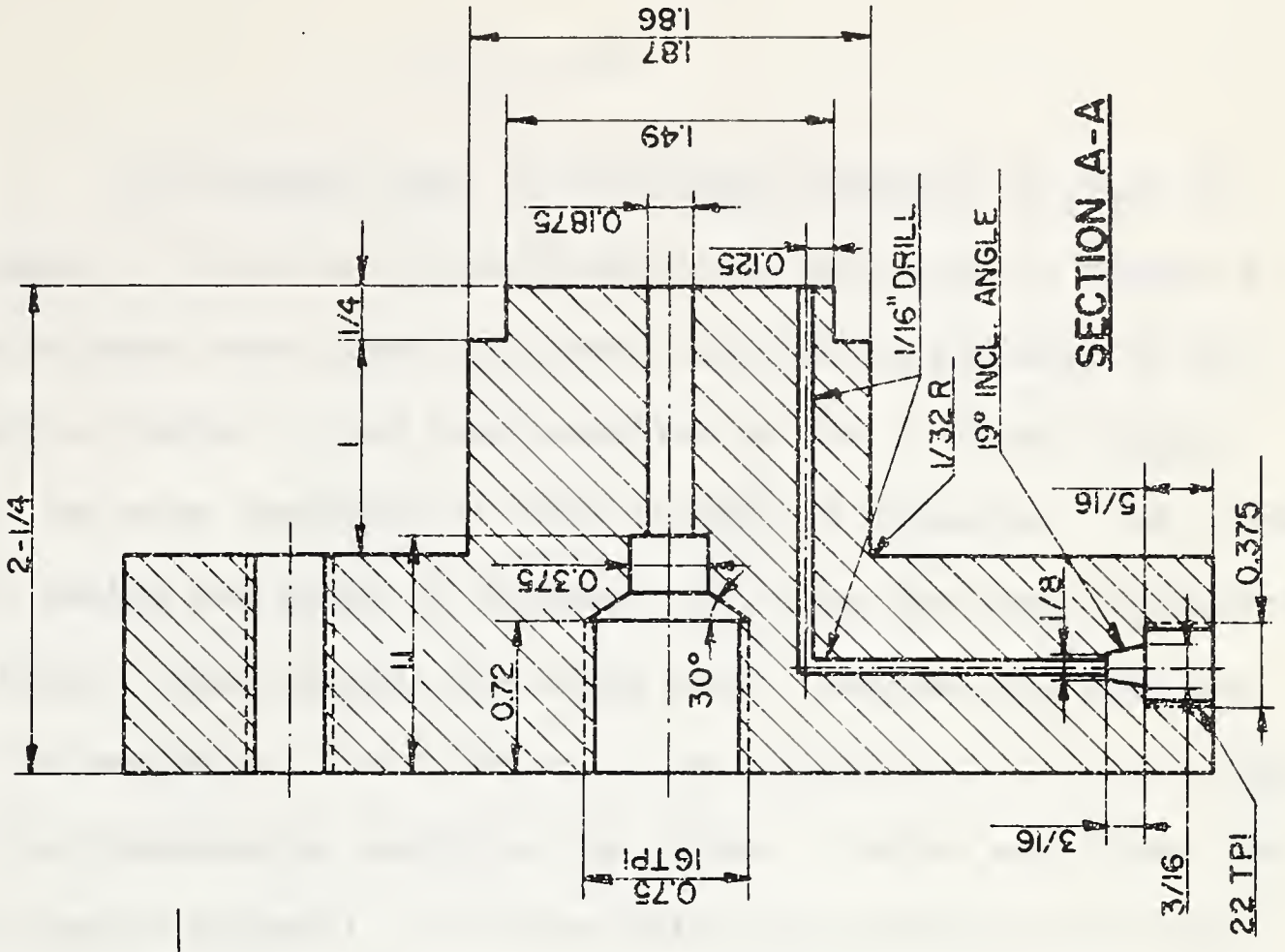
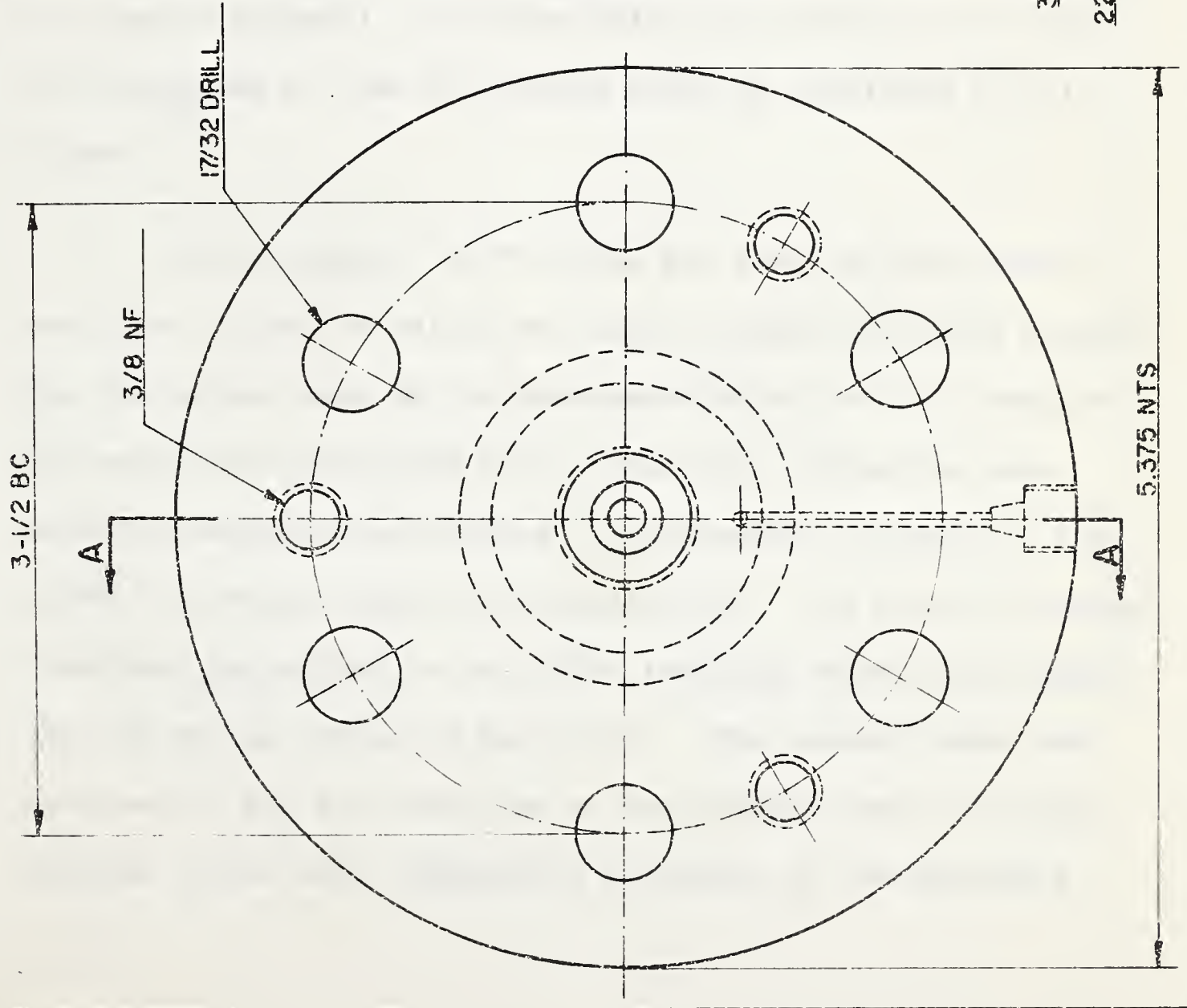
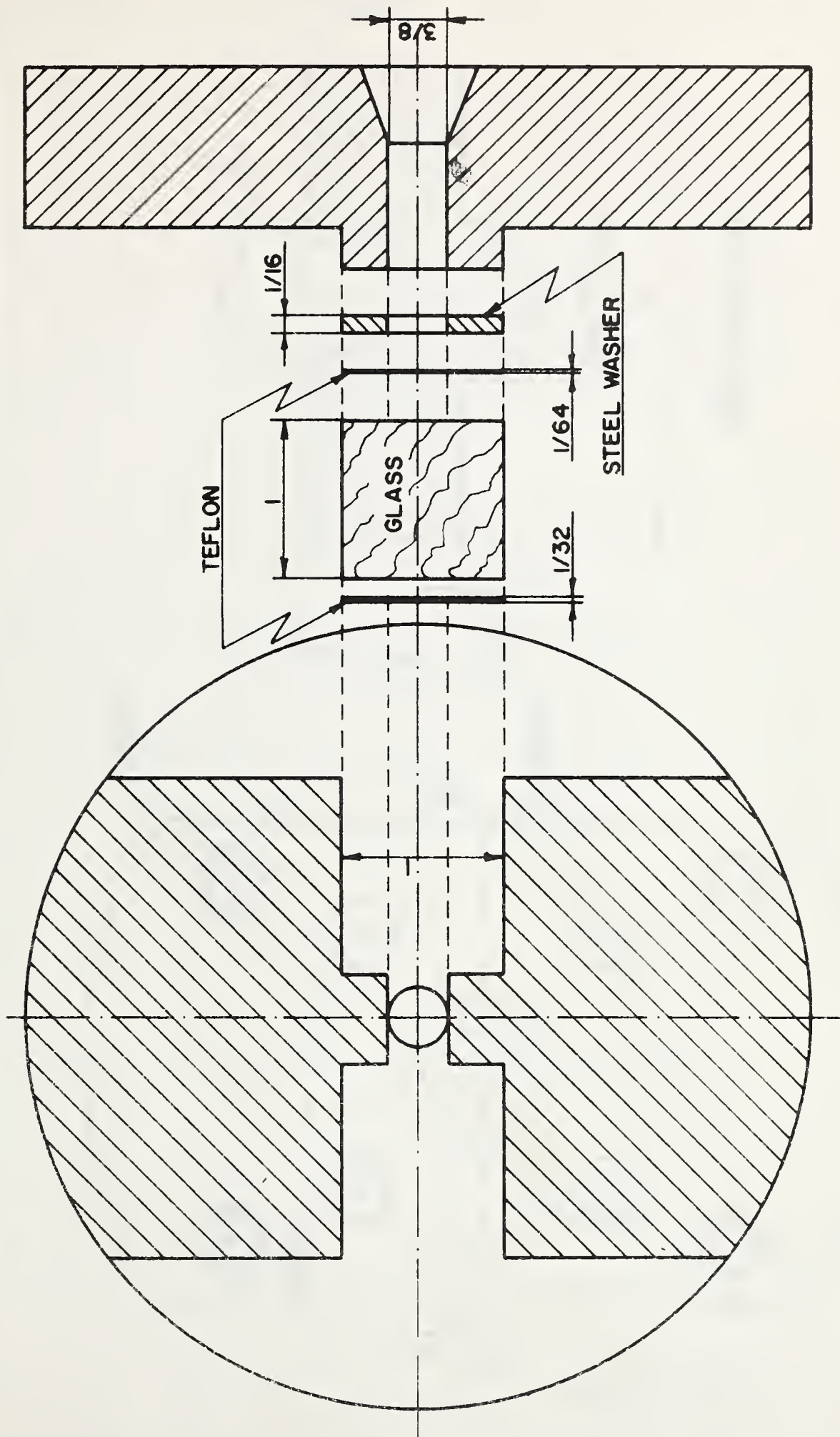


FIG. 6. BOTTOM END PLATE

An exploded view of the window assembly is shown in Figure 7. Details of the cover plate are shown in Figure 8. The windows were glass cylinders one inch in diameter by one inch in height. They were supplied by the J. Unertl Optical Co. and were specified to take 10,000 psi pressure. The cylindrical design was found by Bridgman (8) to be the most satisfactory, although other designs are often used. Because the cell was to be evacuated in the course of the experiment, it was decided to use compression seals on the window. Teflon was chosen for the gasket material. A teflon shim was provided on the top of the window so that the window would be cushioned at all times.

(ii) Piston An "O" ring was used for the piston seal and a rider of teflon was used to keep the piston aligned. The piston was made of the same material as the cell because of temperature expansion and contraction. Using the same material necessitated plating with chromium that part of the piston in contact with the cylinder wall. The piston reference level was determined by initially locating through the window the pin on the bottom of the piston. The conical shape was machined to fit into the cone at the drainage end of the gas section of the cell, permitting reduction of the operating



CROSS SECTION OF CELL (not to scale)

FIG. 7. EXPLODED VIEW OF WINDOW ASSEMBLY

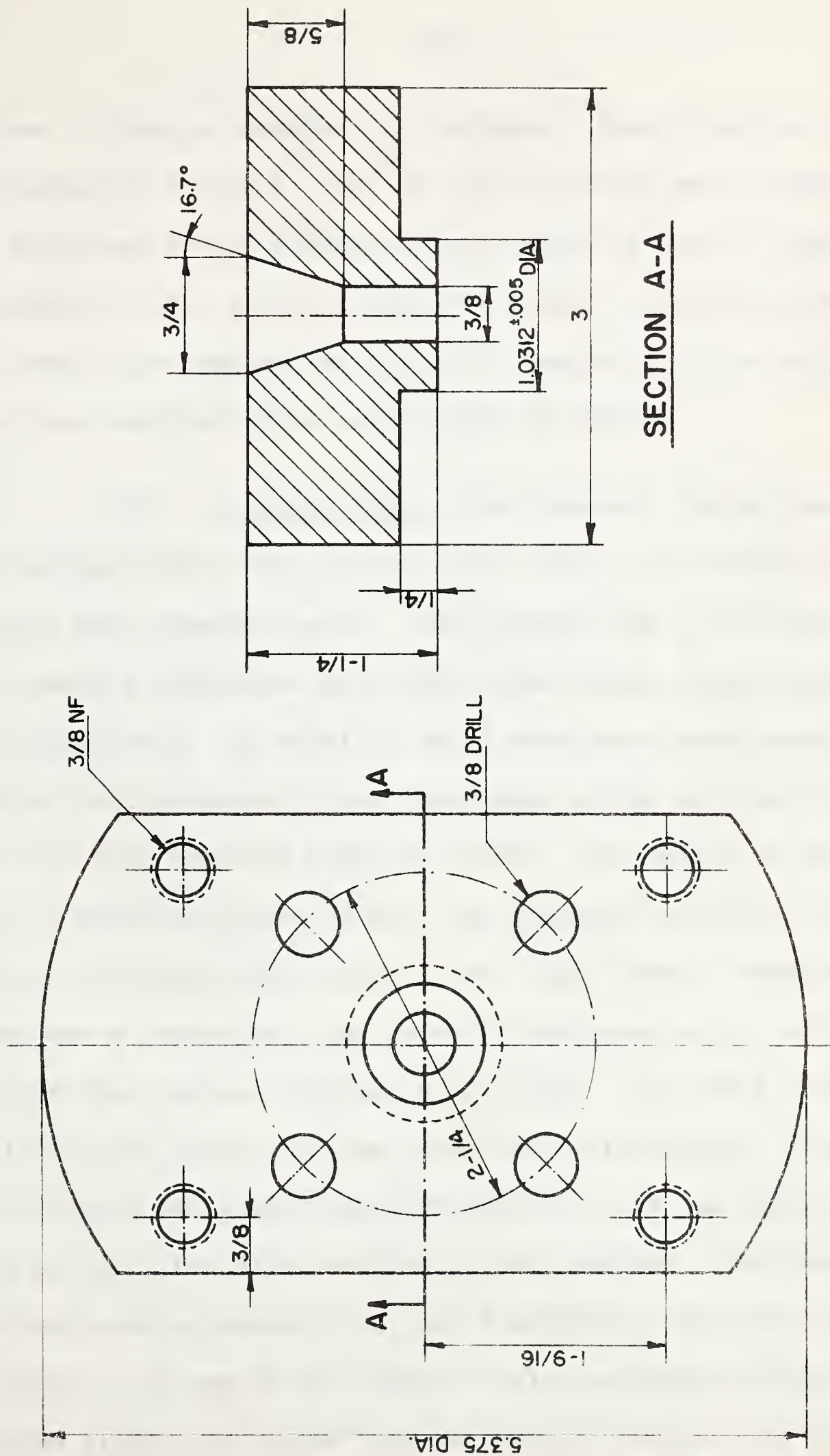


FIG. 8. WINDOW COVER PLATE

volume of the gas section to a minimum. Details of the piston are shown in Figure 9. The two extra grooves were a result of experiments with different positioning of the "O" ring to determine if the teflon rider were needed. They also served to reduce the area of the piston in contact with the cylinder wall and provided for a second seal if needed.

(iii) Internal Valve The internal "valve" was made by welding a 3/16 inch rod onto the stem of a standard 3/8 inch Aminco High Pressure valve. This enabled use of the whole Aminco assembly except the valve body, the bottom plate acting as the valve body. To obtain a spray some experiments were conducted and from them it was found that a hole at least as small as 1/16 inch diameter would be needed. The design of the "valve" tip is shown in Figure 10 with the entrance to the 3/8 inch bore of the cell being used as the "valve" seat. Because 1/16 inch was a convenient size to drill the spray hole, only the tip of the hole was reduced to 1/32 inch. (In tests with the cell top and piston out the spray was satisfactory.) The stem was drilled vertically and horizontally, with the cone threading on until the holes drilled in both matched. The back-up nut was used to prevent the cone from moving from the "open" position. By use of the "Aminco" valve mechanism in the cell bottom plate, the "valve" can be removed from the "seat" result-

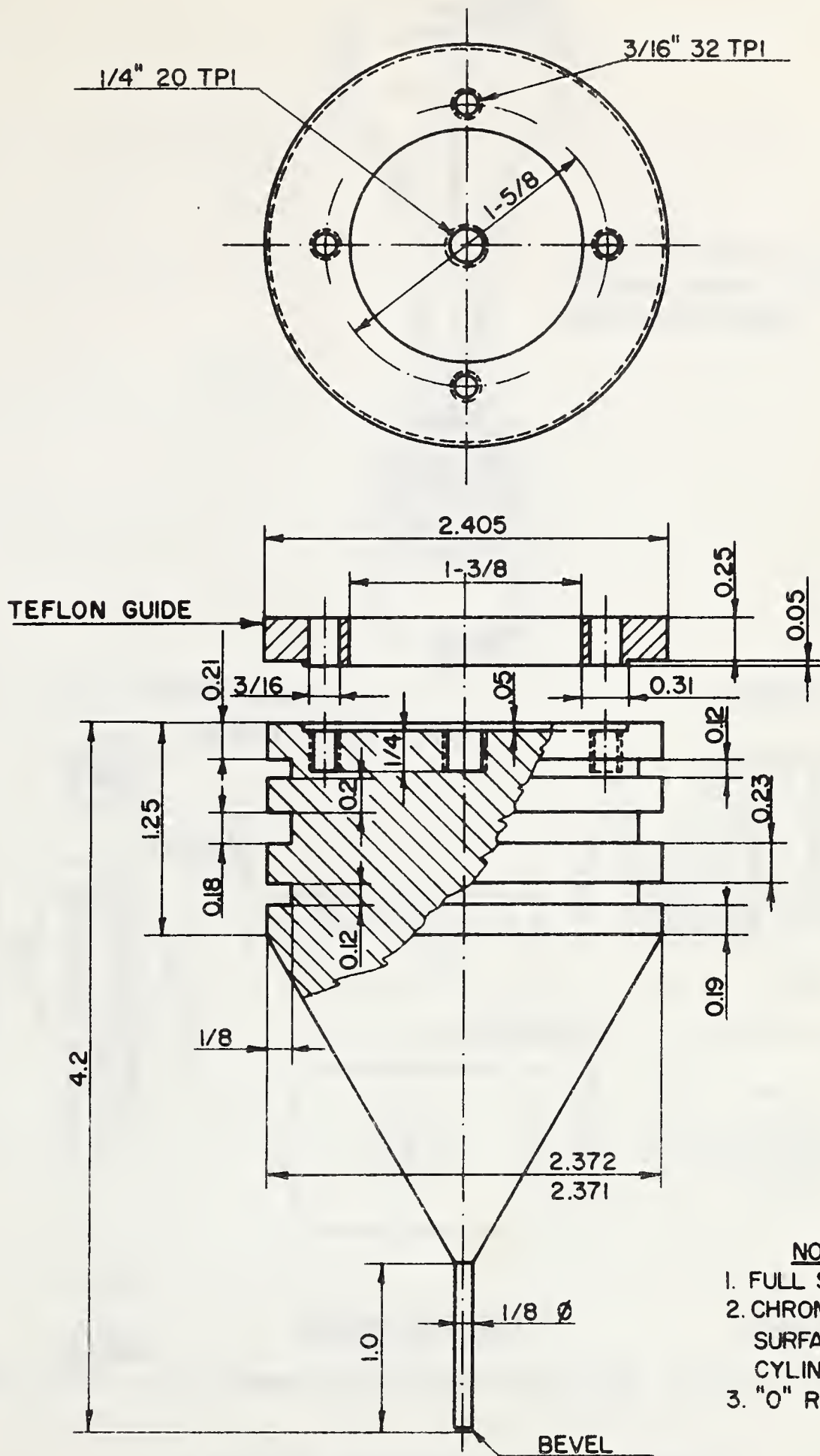
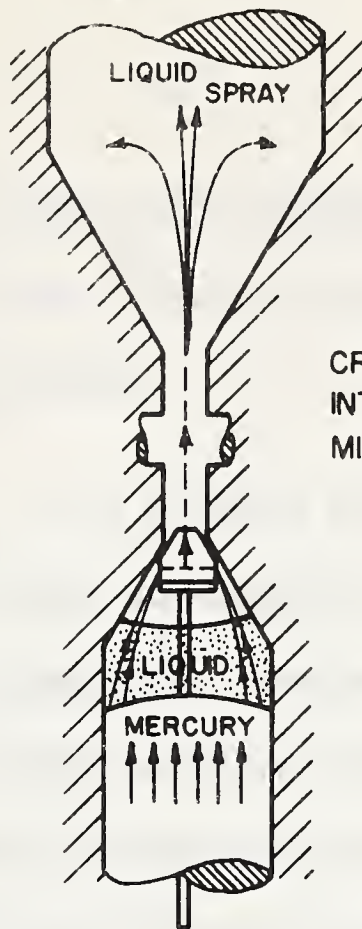
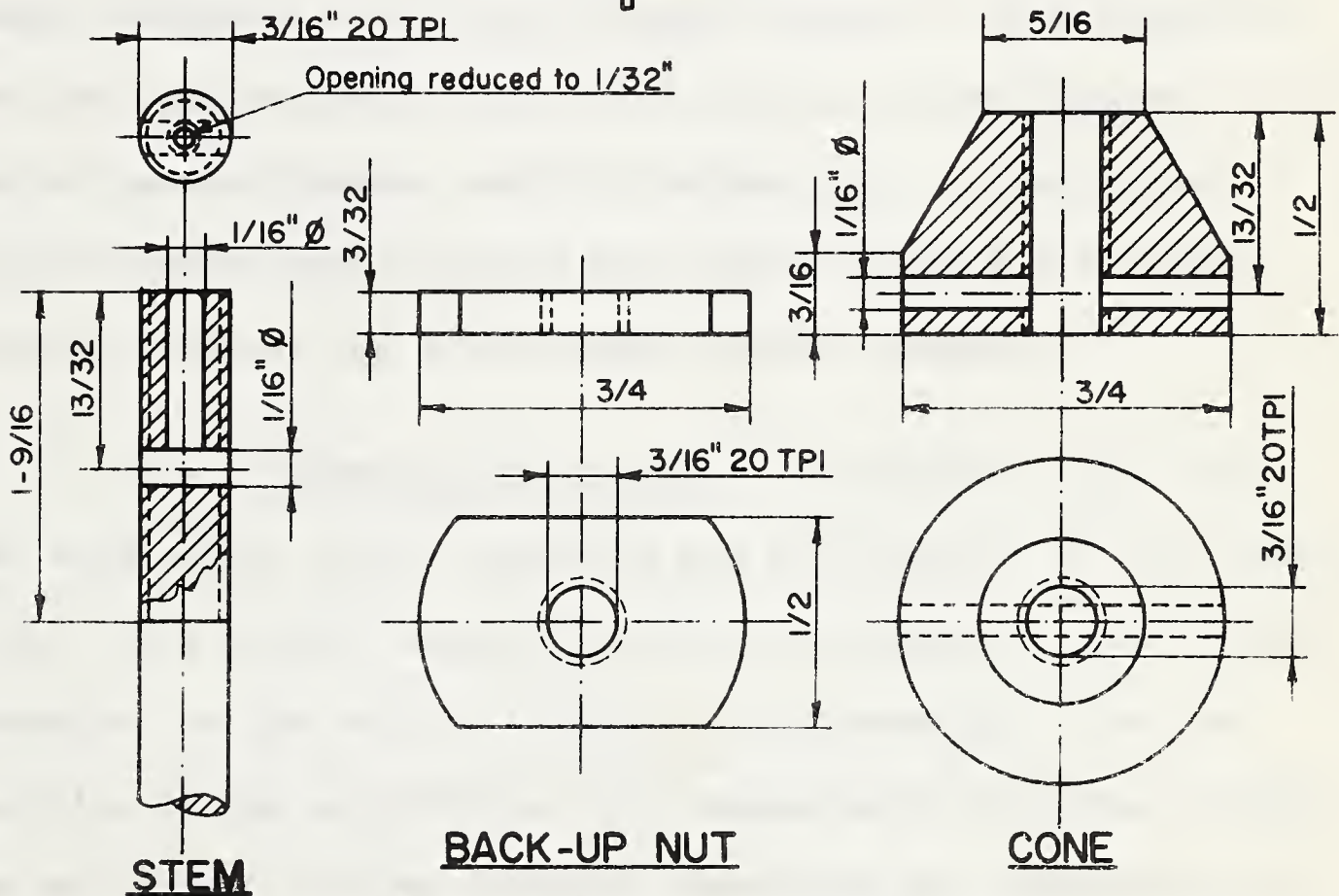


FIG. 9. PISTON DETAIL



CROSS SECTION OF CELL AT
INTERNAL VALVE TO ILLUSTRATE
MIXING MECHANISM



Weld STEM to 5/16" AMINCO High Pressure Valve Stem to Length = 7" Overall

FIG. 10. INTERNAL VALVE DETAIL

ing in a pressure drop lower than through the 1/32 inch hole. Transfer of interfaces could then be carried out with a minimum pressure change in the system.

(iv) Gaskets All gaskets in the cell were made of teflon, which has been used successfully in many other high pressure seals of the same type. Teflon is inert, softer than the hard plastics, yet less resilient than rubber. It is easy to machine to custom specifications. The stepped confined gasket design was chosen for the end closures. Dimensions of the top closure gasket were 2.745 inches outside diameter, 2.375 inches inside diameter and 5/32 inches thick. The bottom closure gasket was also 5/32 inch thick, being 1.870 inches outside diameter and 1.495 inches inside diameter.

(v) Thermocouple Assembly A pressure tight seal was achieved by silver soldering the hot junction of the thermocouple into a short section of 3/16 inch stainless steel tubing connected to the cell by an Aminco male connector. The hot junction of the equilibrium cell thermocouple projected through the cell wall into the interior, measuring the temperature of the contents directly. The thermocouple section is shown in Figure 3. The location in the bottom section was necessitated

because of the use of a piston in the top section of the cell and the desire for the thermocouple to protrude into the mixture for more accurate measurement.

3 AUXILIARY APPARATUS

(a) Double-Acting Mercury Pump

The assembly drawing of the double-acting pump is shown in Figure 11. Figure 13 is a photograph of the pump in place in the apparatus rack (the right-hand cylinder is not visible). Figure 12 shows the dimensions of some of the important parts of the assembly. The cylinders were made 2 11/16 inches in outside diameter and 1 3/8 inches in bore diameter. The cylinder was designed with a safety factor of 2.4 calculated according to the Von Mises criterion for elastic yield. A piston diameter of 1.365 inches allowed a volume displacement of about 245 cubic centimeters. The packing consisted of teflon Chevron-type rings. The drive assembly is a No. 1085 worm gear jack manufactured by Duff-Norton Company. The volumetric scale is graduated in divisions of 0.01 cu cm.

(b) Micrometer Sample Pump

The total volume of the micrometer sampling pump is

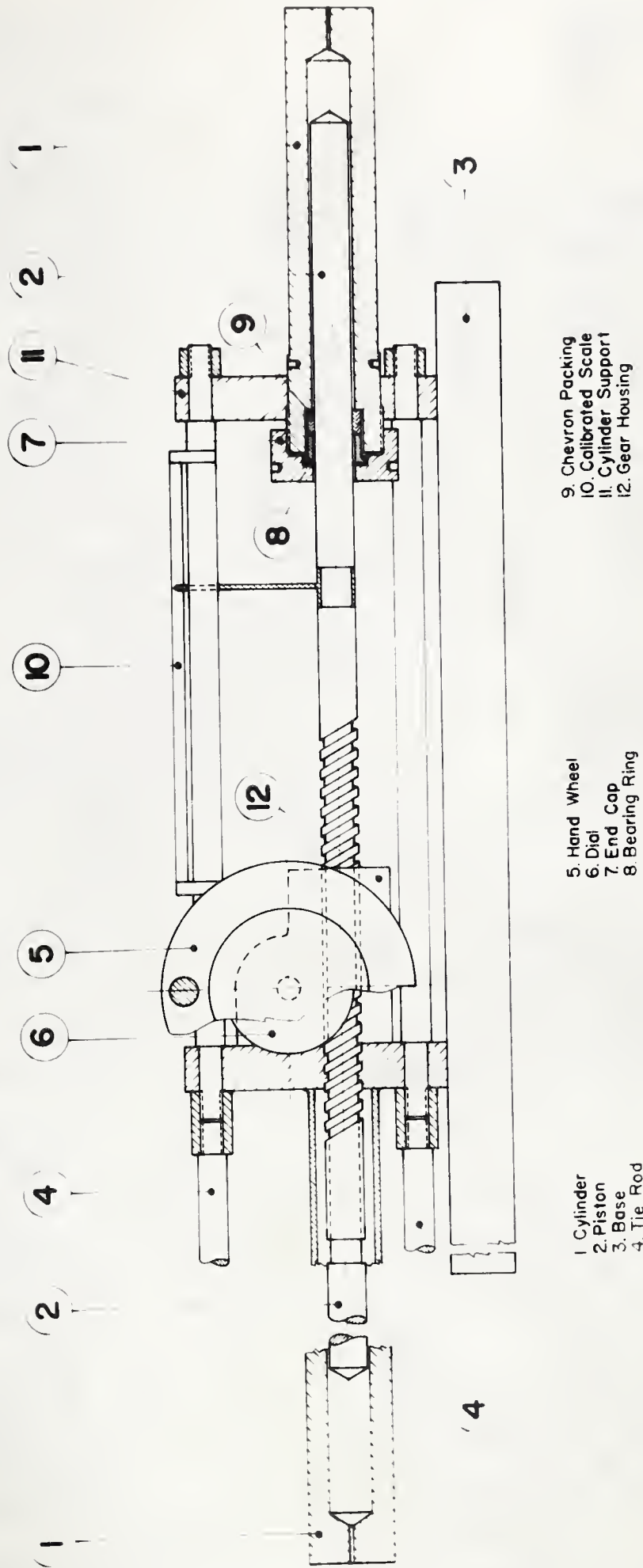


FIG. II. DOUBLE - ACTING PUMP ASSEMBLY

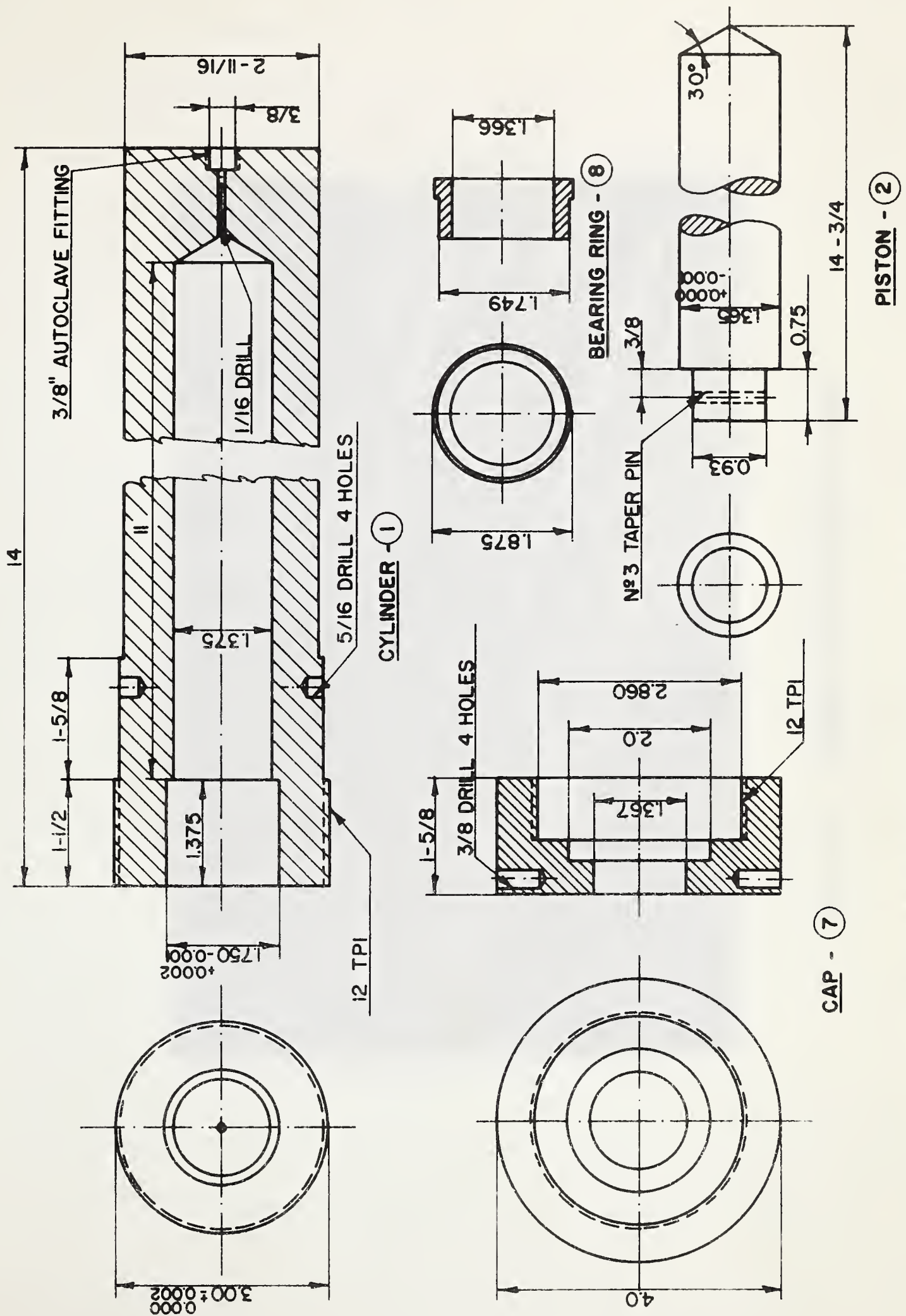


FIG. 12. PUMP PISTON AND CYLINDER DETAIL

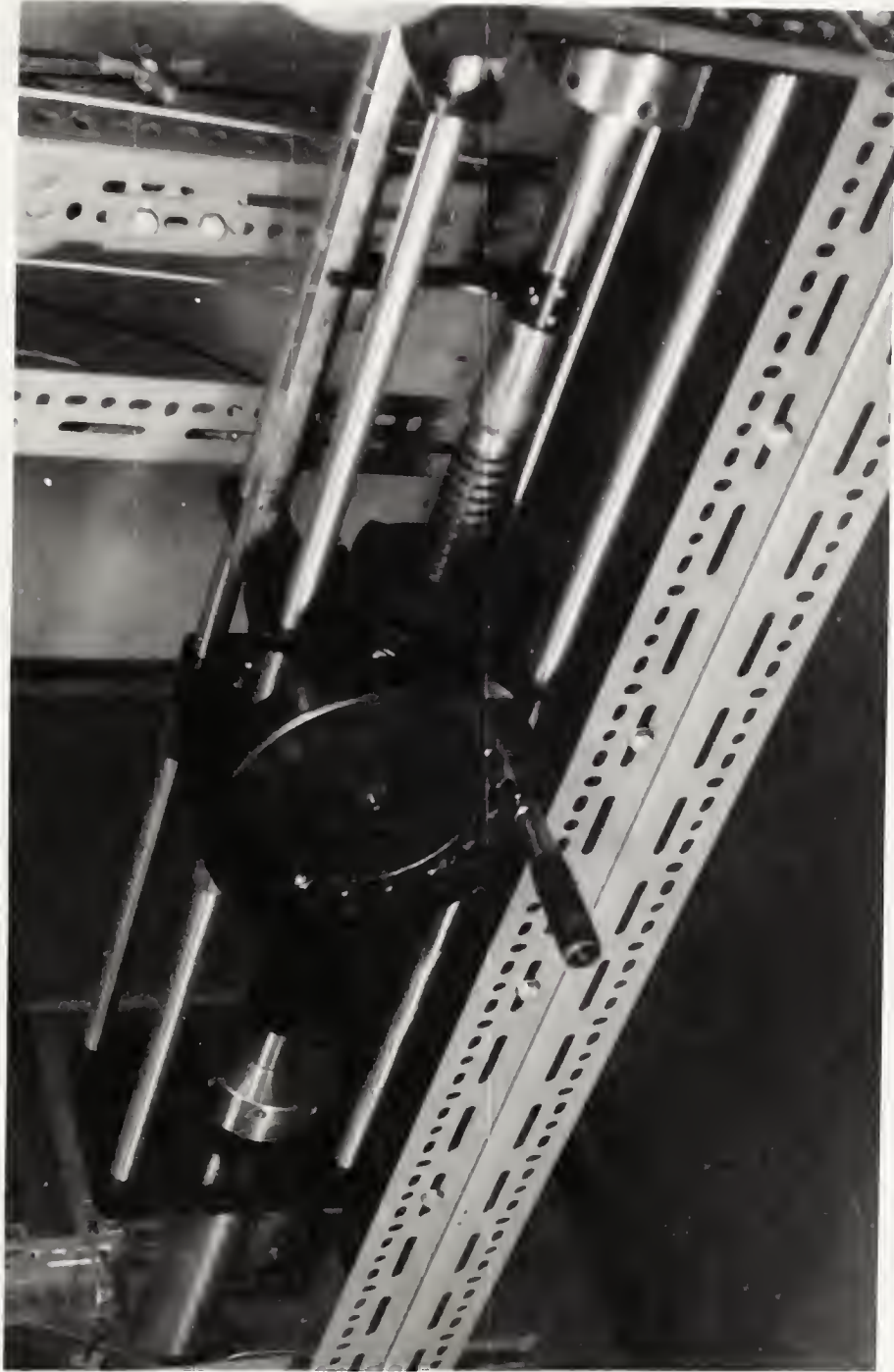


Fig. 13 DOUBLE-ACTING PUMP IN PLACE

approximately two cubic centimeters, the scale being calibrated to 0.001 cu cm. Figure 14 is an assembly drawing of the pump while Figure 15 shows details of some of the parts of the pump. The Humble Oil Co. supplied the original design of the pump, rated to 8,000 psi. To facilitate the present use, a few changes have been made in the design. The packing of the cylinder has been changed to that shown in Figure 15. The piston and cylinder were made of 316 type stainless steel with the bearing nut being of mild steel to eliminate sources of galling. Adapters were provided to permit Ermeto type fittings to be used.

(c) Temperature Bath

The temperature of the cell was controlled by circulating oil, Voltesso 35, from an auxiliary temperature bath through the temperature bath containing the cell. A bimetallic strip controller in the auxiliary bath was used to govern the heater and refrigerator unit. The temperature bath designed to contain the cell was made eleven inches in diameter and twenty-four inches high. A section of the bath is shown in Figure 16. The wall was made from 20 gauge stainless steel while the bottom was made from 1/8 inch stainless steel plate to support the weight of the cell. Seals for the internal valve stem and 1/8 inch

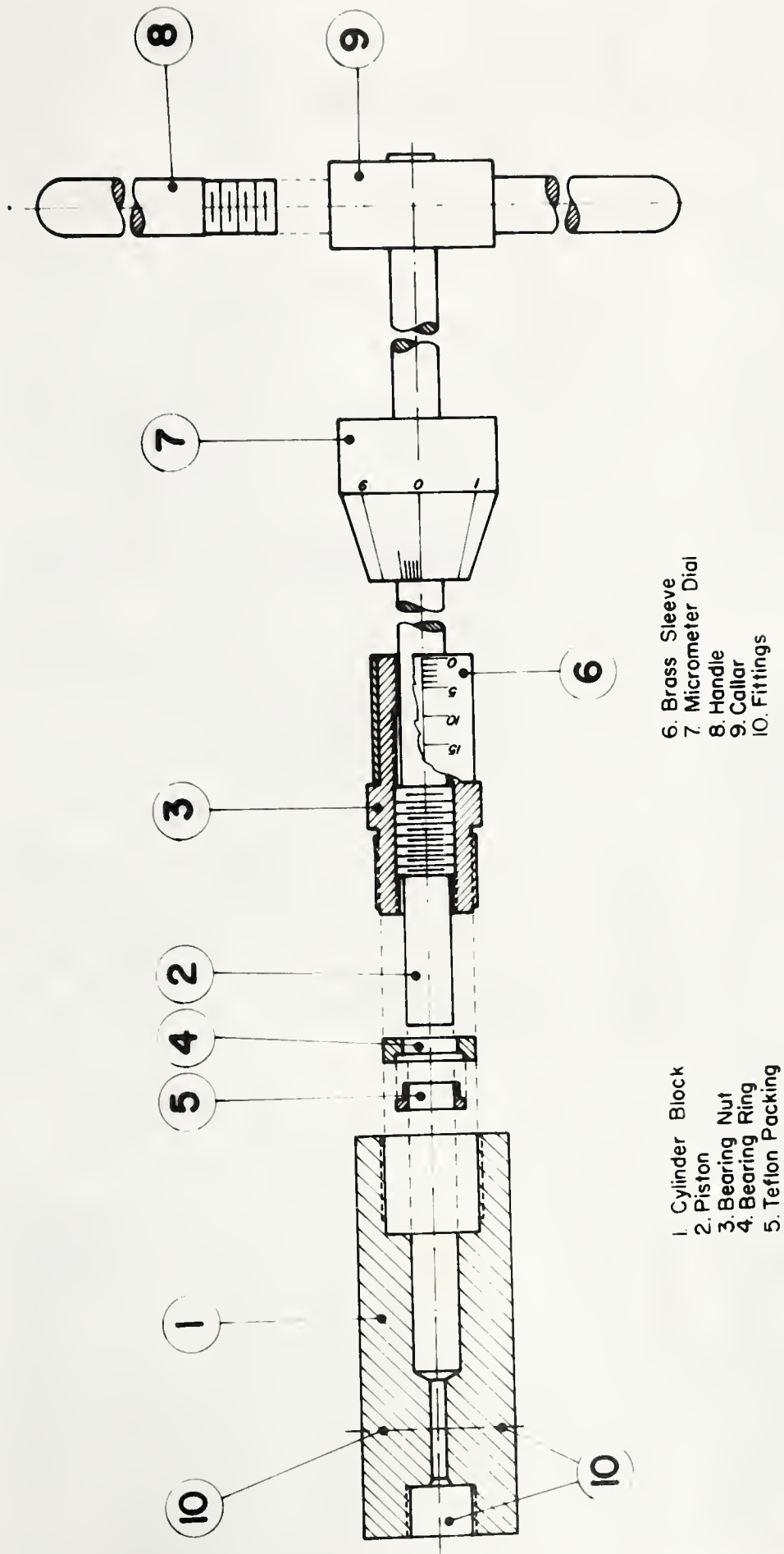


FIG. 14. MICROMETER PUMP ASSEMBLY

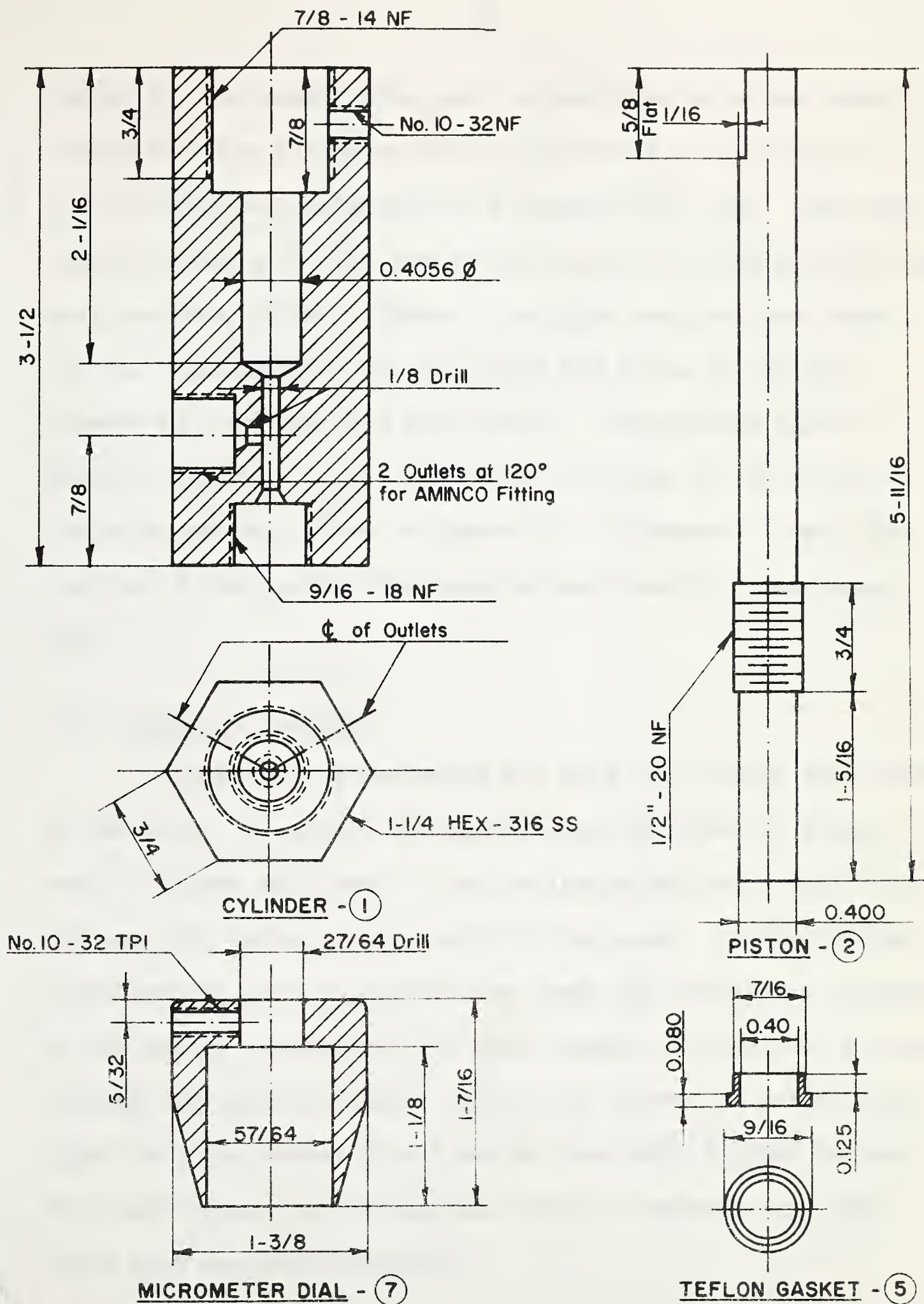


FIG. 15. MICROMETER PUMP DETAILS

tubing for the sample line were accomplished by using copper tubing fittings silver soldered to the bath. The farrel in the fittings was replaced with a neoprene "O" ring. The cell supports were made from hexagonal brass rod to which brass ring sections were silver soldered. The ring sections were made to fit the circumference of the bottom end plate of the cell closely to hold the cell positioned. Circulating fluid is passed through one-half inch copper fittings in the bottom of the bath and is allowed to flow with a differential head from the top of the bath to the pump through one-half inch copper pipe.

(d) Periscope Assembly

A periscope arrangement was used for viewing the inside of the cell. A section of the periscope is shown in Figure 17. Two 45° prisms were used in the periscope and were sealed from the bath oil using a clamp and "O" ring seal. A cathetometer telescope was used to magnify the image and facilitate focusing on the desired section of the cell interior. Light was provided through the opposite window using a 45° mirror to reflect the light into the window from a hollow tube with a glass bottom. The light source was an American Optical Company microscope light with variable intensity.

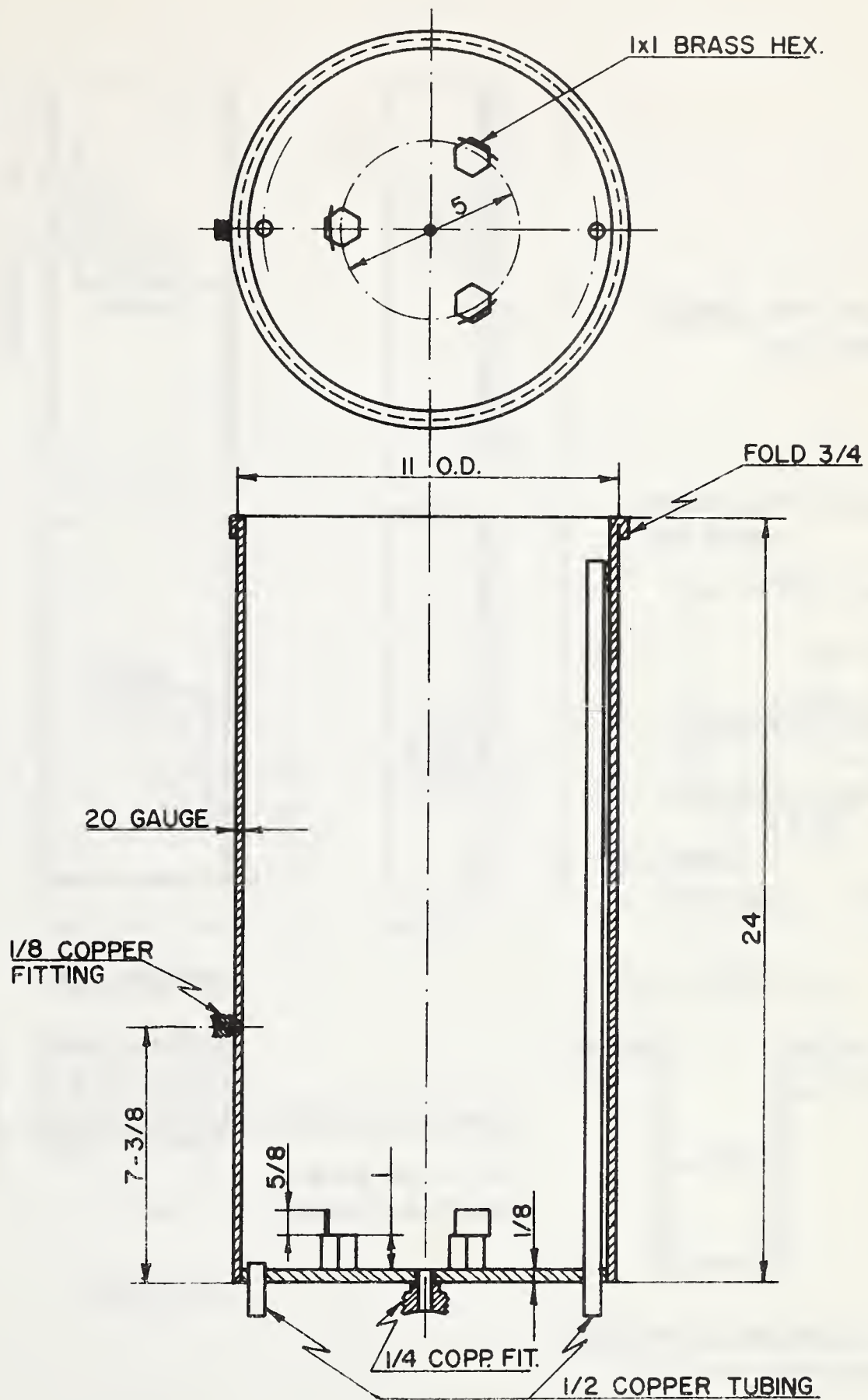
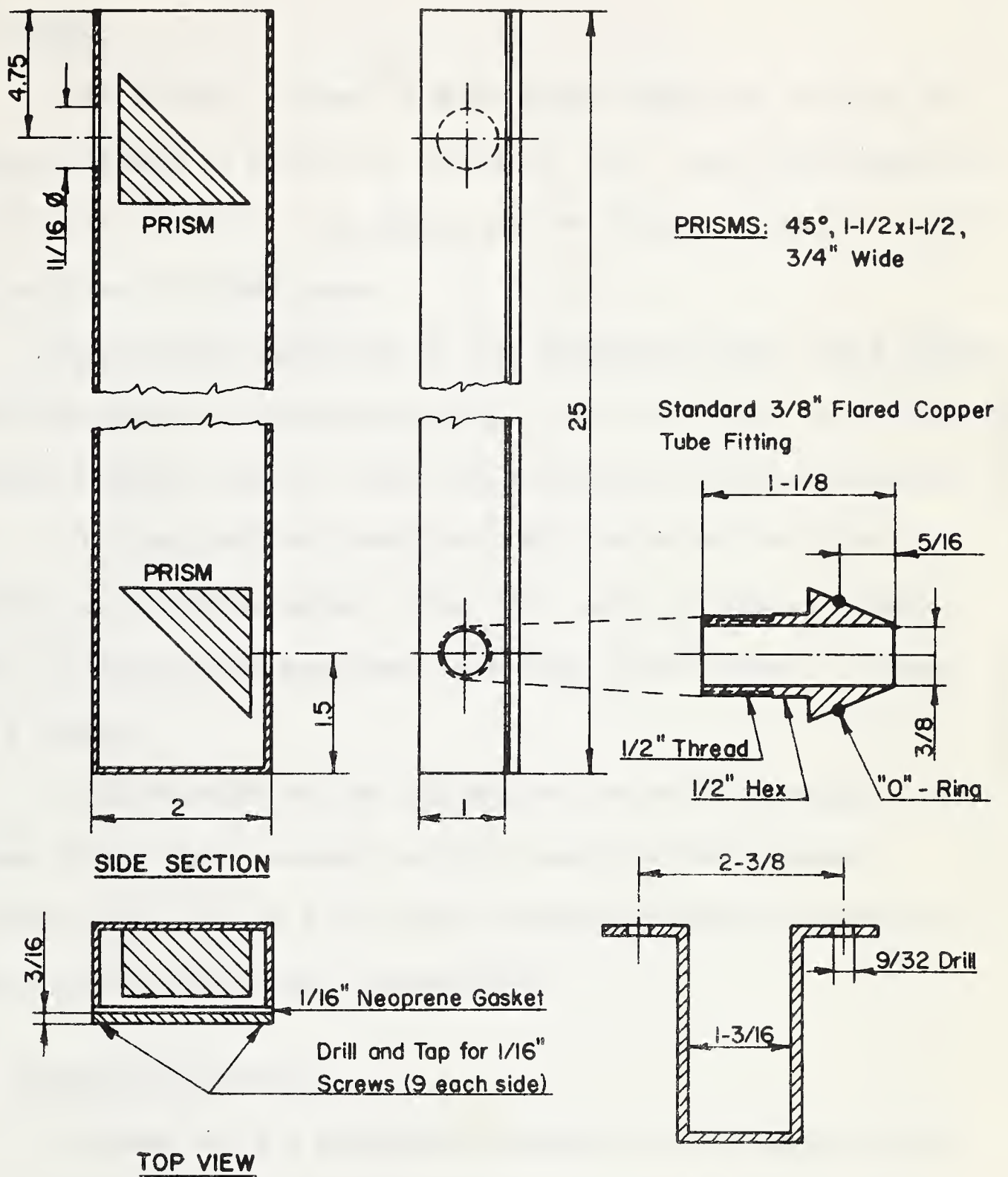


FIG. 16. TEMPERATURE BATH



Note: Drill and Tap Window Cap 1/4" 20 TPI to fit Periscope Bracket

FIG. 17. PERISCOPE ASSEMBLY

(e) Other

The tubing, valves, and fittings were made of type 316 stainless steel by Autoclave Engineers Inc. and were rated for 15,000 psi at 100°F. The tubing had an outside diameter of 1/8 inch with a 1/16 inch bore.

The driers consisted of two Jerguson liquid level gauges made from type 316 stainless steel. One was filled with anhydrous calcium chloride and the other with Drierite (calcium sulfate).

Two gas holders rated for 1800 psi were installed for storing the purified gases. They were made of 304 stainless steel by the Hoke Company and consisted of two sizes, 1 litre and 3 litres.

The pressure of the system was varied by changing the volume of the cell contents using a positive displacement mercury pump. It had a 100 cubic centimeter capacity and was made by Ruska Instrument Corporation.

(f) Assembled Apparatus

Figure 18 is a schematic drawing of the overall equipment assembly. The apparatus was fastened to a dexion frame suspended from the ceiling. Figure 19 shows the assembled equipment on the frame.

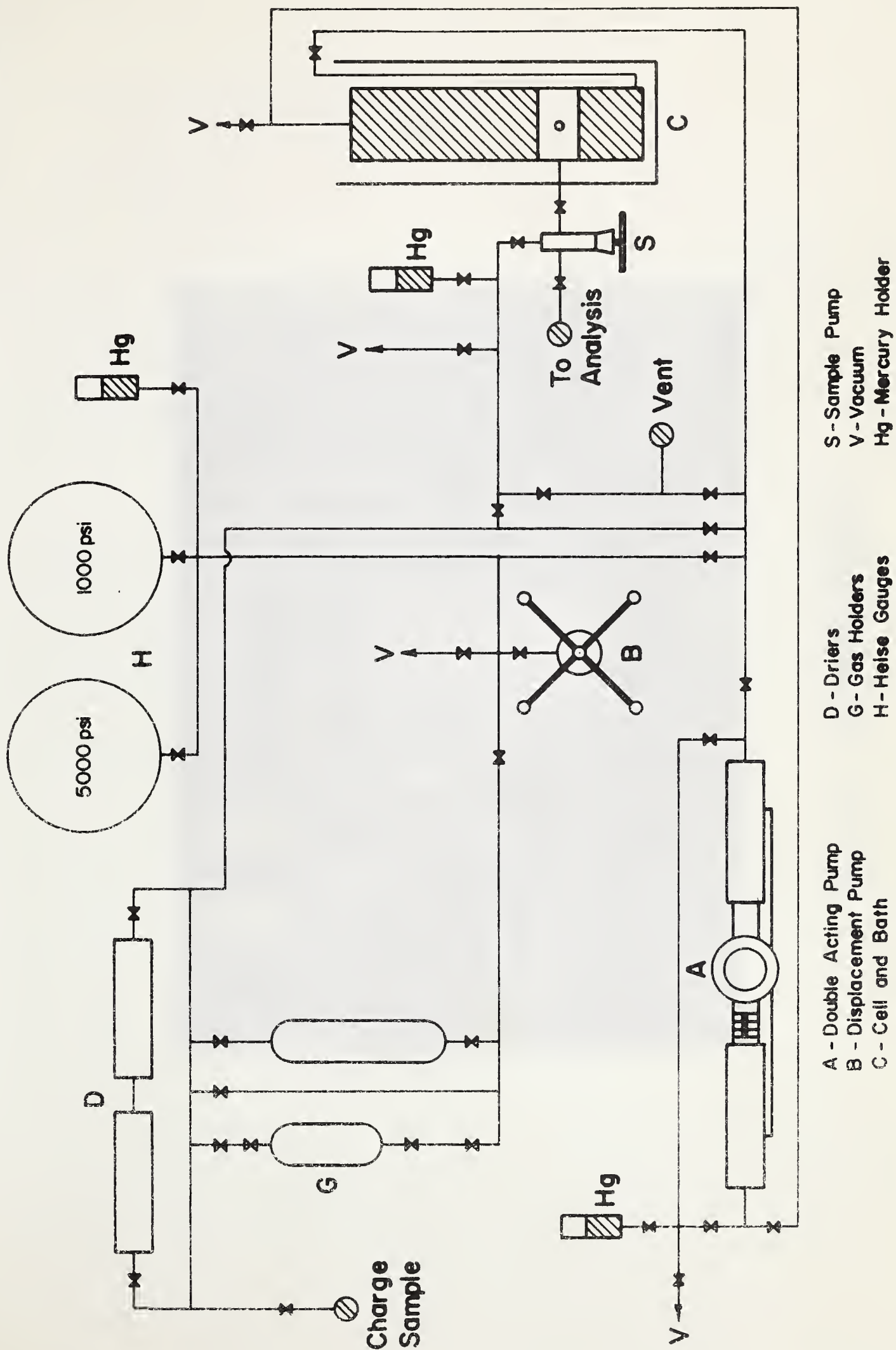


FIG. 18. SCHEMATIC DIAGRAM OF EQUIPMENT



Fig. 19 ASSEMBLED EQUIPMENT

4 CALIBRATION OF APPARATUS

(a) Temperature

The temperature of the cell contents was measured using an iron-constantan thermocouple and a Leeds-Northrup Model K-2 potentiometer. The thermocouple was calibrated against a platinum resistance thermometer standardized by the United States National Bureau of Standards. A Leeds-Northrup Mueller Bridge and a Leeds-Northrup Model K-3 potentiometer were used in conjunction with the standard thermometer to obtain a calibration to $\pm 0.02^{\circ}\text{C}$ for each point from -10°C to $+200^{\circ}\text{C}$. Figure 29 of Appendix II shows the calibration curve obtained.

(b) Pressure

The pressure in the system was measured using a 1000 psig Heise bourdon tube gauge and a 5000 psig Heise bourdon tube gauge. The Heise gauges were calibrated in situ to ± 0.5 psig and ± 5 psig respectively or $\pm 0.2\%$ whichever is the largest. Air was used in the lines and gauges to establish the zero points of the gauges. The lines and gauges were then evacuated and filled with mercury, the difference in the air and mercury readings providing the effect of the head of mercury on the pressure. The reference level of the dead weight gauge was permanently

established for subsequent pressure measurements. Figure 30 in Appendix II shows the calibration curve for the 100 psig gauge. The 5000 psig gauge was calibrated only to 2500 psig and showed no deviation from the scale reading greater than the errors stated above.

(c) Volume

In order to measure volumes of the sample in the cell accurately, a calibration was obtained on the double-acting pump and the displacement pump by weighing mercury displaced for incremental scale displacements. Figure 31 in Appendix II shows the volumetric calibration at room temperature of the double-acting pump. The accuracy of these calibrations was estimated to be ± 0.005 cu cm, while the maximum cumulative scale deviation for the displacement pump was found to be -0.169 cu cm. It was found that pressure had no measurable effect on the volume measured by the displacement pump up to 3000 psi. This pump was used as the standard in determining the effect of temperature and pressure on the cell volume. It was found that the total cell volume expanded 0.02 cu cm per °C. The effect of pressure at room temperature is shown in Figure 32 of Appendix II.

(d) Chromatographic Analysis

The chromatographic columns were calibrated using samples of known composition, while holding the instrument variables constant. A calibrated 100 ml gas burette was employed to prepare these samples, corrections being applied for the difference in compressibility factors of the gases used. The calibration for methane-n-butane mixtures is shown in Figure 33 of Appendix II. A quantitative measure of the composition was obtained by multiplying the peak height by the peak width at one-third the peak height. The "areas" thus obtained for each component were summed and the fractional "areas" of n-butane were obtained for each mixture and plotted versus the actual mole fraction of the sample. For the hydrogen sulphide-n-butane mixtures, calibrations of peak height with mole per cent were obtained and are shown in Figure 34 of Appendix II.

D EXPERIMENTAL TECHNIQUES

1 ASSEMBLY OF THE CELL

The actual assembly of the cell, and in particular the windows, provided more difficulty than had been initially anticipated. All the bolts used in the cell were cleaned and lubricated before assembly. The bolts on the top and the bottom end plates were tightened with a torque wrench to 40 foot pounds torque each. This torque was adequate for the pressures used. It was found that the bearing nut for the internal "valve" assembly worked loose with use, necessitating the use of a retainer which was fastened to the bottom plate after the nut had been inserted.

A number of experiments were performed with the window assembly in order to determine a suitable design. In the original design, gaskets of teflon, 1.06 inches in outside diameter, 0.48 inches in inside diameter and 0.075 inches thick were used to cushion the glass on both inside and outside surfaces. Due to cold flow of teflon, the compression of the gasket was reduced after tightening, resulting in a leak at about 3500 psi. Another

result of the gasket extrusions was a reduction in the area of vision.

To circumvent the gasket extrusion problem, harder gaskets were used. Asbestos impregnated with graphite was the first hard gasket material tried. However, it was also the first gasket material with which a glass window was broken. One glass was broken during the assembly and another was broken one day after assembly while pressure testing. Examination of the window-well seat showed that the bevel allowed for stress relief at the seat extended past the circumference of the glass with the result that only a line contact was made at the seat. Consequently, the extended bevel was removed. Gaskets made of Phenolite, a relatively hard plastic, linen reinforced, were the next type to be tried. The remaining two glasses of the first shipment were broken with these gaskets in use. Because the four windows had broken a critical examination of the assembly and assembly techniques was undertaken.

After the first two breaks, the four glasses were examined under polarized light. There was some stress concentration in the two intact glasses but it did not explain the breaks. The last two breaks showed a similar pattern to the first two. One crack in each set extended for only half the length of the glass

cylinder, from the interior face to the centre of the glass. The window seat was re-examined, this time revealing a machining ridge left from the bevel removal. As a result the seat was hand-lapped and polished with jeweller's rouge to ensure an even surface.

Two steel plugs the same size as the glass windows were machined and used for further tests with gaskets. Prior to the lapping of the window seats, lead impressions were obtained of the top and bottom of both window assemblies. Seat discontinuities were revealed on the lead impressions. Also revealed was the fact that the bearing surface of the window plate was not centred, i.e. the bolt holes in the cell body were not drilled concentrically with the window port. To correct this error, the holes in the plates were enlarged, washers being used under the heads of the bolts. A 1/16 inch steel bearing ring was inserted next to the plate to provide a wider bearing surface. The plate protrusion was wrapped with teflon tape to provide for centring. Each face plate was scribed with centre lines, as was the cell body, to aid in alignment of the plates.

With the steel plugs inserted instead of the glass windows, the cover plates were torqued down without the bracing bolts being used. No bending of the plate was observed to a torque

on each bolt of 50 foot pounds. As a consequence, the bracing bolts were no longer employed. Gasket extrusion was also examined with steel plugs in place, rubber and teflon being used. Rubber was not satisfactory, but it was found that thinner teflon could be used. The resultant dimensions of the bottom gaskets were 0.04 inches thick, 1/2 inch inside diameter and 15/16 inches outside diameter. The top gasket cushion was 1/64 inches thick, 1/2 inch inside diameter and 1.06 inches outside diameter. For centring purposes the steel plugs and eventually the glass, were bound with two bands of teflon tape, 1/4 inch wide.

The final assembly of the windows was accomplished after the above changes were made. A torque wrench was used to tighten the bolts to 20 foot pounds torque. In all cases of window assembly, feeler gauges were used to establish that the plate was being tightened parallel to the window seat. Although the cell pressure after assembly has been limited to 2400 psi, a working pressure of 3000psi might be possible without a leak occurring.

2 PREPARATION OF SAMPLES

The n-butane used in the experiments was prepared by distillation in a Podbielniak low temperature distillation

apparatus, using a reflux ratio high enough to enable good separation of the n-butane from the iso-butane. The n-butane was then frozen into distilling flasks which are illustrated in Figure 20. Liquid nitrogen was employed as the coolant. Next, the flasks were evacuated, the n-butane vaporized and then used to purge the flasks. The procedure of freezing, evacuating and purging was followed two or more times until chromatographic analysis showed that the air content was reduced to the level desired. Before entering the cell the gas was passed through the driers to remove any water remaining. The methane was considered of adequate purity and was passed through the driers directly from the supply cylinder at cylinder pressure. The hydrogen sulphide was drawn from the liquid phase and then passed through the driers to the cell. No other treatment of the hydrogen sulphide was attempted.

The methane was obtained from the Phillips Petroleum Company with a specified purity of 99 mole percent minimum. The n-butane was a commercial grade supplied by courtesy of Imperial Oil Company and was about 92 percent n-butane. After purification, the n-butane was analyzed by the chromatographic method to be at least 99.9 mole percent n-butane. The hydrogen sulphide was supplied by the Matheson Company and was stated

to be 98.8 percent pure. Using the driers and drawing the sample from the liquid phase improved the purity to at least 99.0 mole percent.

3 CHARGING OF THE CELL

The sample was charged to the cell through the sample outlet via the driers. Provision was also made to allow charging via the driers and into the lower section of the cell. Depending on the supply pressure of the charge, the cell was either kept at operating temperature, or cooled to allow condensation of the incoming gas and permit more sample to be charged.

4 ATTAINMENT OF EQUILIBRIUM

The following procedure was employed to mix the gas and liquid contents of the cell. The liquid was lowered below the internal valve using the double-acting pump. The internal valve was then closed. With the valve closed, the double-acting pump was used to raise the liquid rapidly enough to spray it into the gas phase. Time was allowed for the liquid to drain down past the sight glass before the procedure was repeated.

Mixing was continued until the pressure remained constant, before and after spraying. An illustration of the spraying step is shown in Figure 10. After the temperature, as indicated by the thermocouple, and the pressure had remained constant, the desired volumes were measured.

5 SAMPLING PROCEDURE

Sampling was considered a most important step in obtaining multicomponent vapor-liquid equilibrium data. Considerable care was exercised to ensure that equilibrium was not disturbed during sampling and that the sample was representative of the contents.

A micrometer displacement pump was used as a method of obtaining a small sample of known volume from the cell. Mercury was added as the sample was withdrawn to keep the volume constant and maintain equilibrium. The fact that small samples were withdrawn was in favor of minimum disturbance of equilibrium.

The following sampling procedure was employed assuming the liquid sample was withdrawn first. The sample line from the pump to the cell was purged with mercury, the mercury being visible as a droplet on the inside of the cell at the sample

line terminal. The liquid level was raised above the window using the double-acting pump. The micrometer pump was then used to withdraw a definite amount of sample, mercury being added to the bottom of the cell at the same rate using the Ruska mercury pump. When enough sample was in the line, two courses could be followed:

- (a) The mercury could be raised, using the double-acting pump, past the window, trapping the sample between slugs of mercury in the line. The sample was then withdrawn into the sample pump.
- (b) The amount of sample needed could be withdrawn past the sample valve, the sample valve closed and the sample processed. The line and pump up to the outlet valve were subsequently evacuated and filled with mercury. The sample line to the interior of the cell was then purged with mercury, the pressure being held constant by removing mercury with the Ruska pump.

When sampling according to procedure (a), the gas sample could be taken directly after the gas was lowered to the sampling level by using the double-acting pump. When sampling according to (b), the first sample of gas obtained should be discarded as not representative, and a second sample obtained and analyzed.

After the sample was isolated in the sample pump, it was expanded to the gas holder where it was mixed, allowed to come to room temperature, the volume measured and then analyzed in the chromatographic apparatus. The gas holder was of the same design as the gas burette on a standard Burrell Orsat apparatus. The sample pump was not thermostated but a heating tape was used to control the temperature of the lines and pump slightly above the cell temperature when sampling the gas.

6 MEASUREMENT OF VOLUMES

Volumes were measured by use of the calibrated pumps. The piston was initially located at the reference level in the window. Subsequent locations were determined from the cylinder volume of the side of the double-acting pump connected to the top of the cell. Volume changes in the cell could be determined by the scale on the Ruska pump, or if necessary by measuring the volume with the double-acting pump, the mercury meniscus being at the reference level. The volume of liquid and gas present could be measured by noting the volumes indicated on the double-acting pump when mercury and liquid respectively were at the reference level in the window.

7 ANALYSIS

A Burrell K-2 "Kromotog" was used to analyze the samples taken from the cell. The column conditions for the analysis of n-butane-methane mixtures were:

Column	:	Apiezon "L" on firebrick
Column Length	:	2.5 meters
Carrier Gas	:	He at 35 ml/min
Detector Current	:	180 ma
Column Temperature	:	Room temperature
Sample Size	:	1 ml

The column conditions for the analysis of n-butane-hydrogen sulphide mixtures were:

Column	:	Tricresylphosphate on Celite (30/70)
Column Length	:	5 meters
Carrier Gas	:	He at 30 ml/min
Detector Current	:	180 ma
Column Temperature	:	Room temperature
Sample Size	:	1 ml

Quantitative results were obtained by calibration of the Kromotog as described in the section on calibrations.

8 MERCURY CLEANING

The mercury used in the equipment was purified extensively so that it could be used with hydrogen sulphide. It has been reported by other investigators that mercury does not react with hydrogen sulphide if water is absent and the mercury is pure.

The mercury was purified by a succession of paper filters, followed by oxidation of impurities in an Oxifier manufactured by the Bethlehem Instrument Company. The mercury from the Oxifier was washed in Benzene to remove any oil in a manner similar to that described in Comings (10). After the mercury was washed it was filtered in a Bethlehem Instrument Company Type F mercury filter operating on the gold adhesion principle. Distillation under vacuum was the final stage in the purification. The mercury used with hydrogen sulphide was run through the still twice.

A few tests were run during which a hydrogen sulphide - n-butane mixture was confined over mercury in glass. No reaction was observed during an observation period of one week. However, after atmospheric air entered the glass receptical containing hydrogen sulphide, reaction occurred resulting in a black scum on the surface of the mercury. This confirmed the importance of keeping the working samples as dry as possible.



Fig. 20 DISTILLING FLASKS

E EXPERIMENTAL RESULTS

1 SYSTEM N-BUTANE-METHANE AT 100°F

Data obtained on the system n-butane-methane are shown in Figure 21 and tabulated in Table 1 of Appendix I. The data has a maximum variation from that of Sage and Hicks and Lacey (60) of + 0.02 weight fraction. Also plotted in Figure 21 is the data of Sage, Hicks and Lacey (60) and of Rigas, Mason and Thodos (55).

2 COMPRESSIBILITY DATA FOR METHANE

Several values for the compressibility of methane were obtained and are shown in Table 2 along with the corresponding data of Olds, Reamer, Sage and Lacey (39). Maximum deviation is - 0.003 in the compressibility factor.

3 THE SYSTEM N-BUTANE-HYDROGEN SULPHIDE AT 100°F

Data obtained on the system n-butane-hydrogen sulphide are shown in Figure 22 and tabulated in Table 3 of Appendix I.

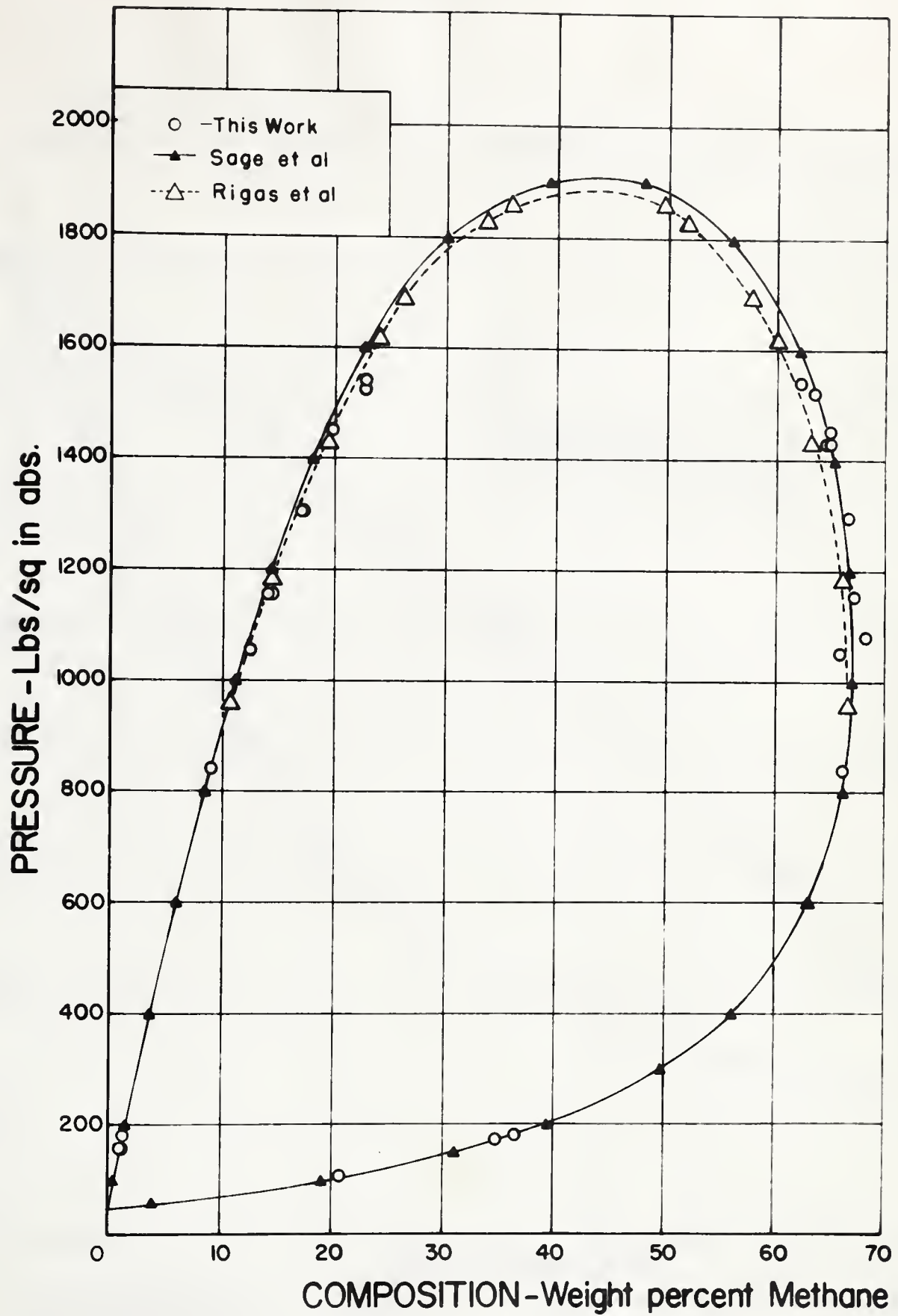


FIG. 21. PRESSURE - COMPOSITION DIAGRAM at 100°F of the SYSTEM n -BUTANE - METHANE

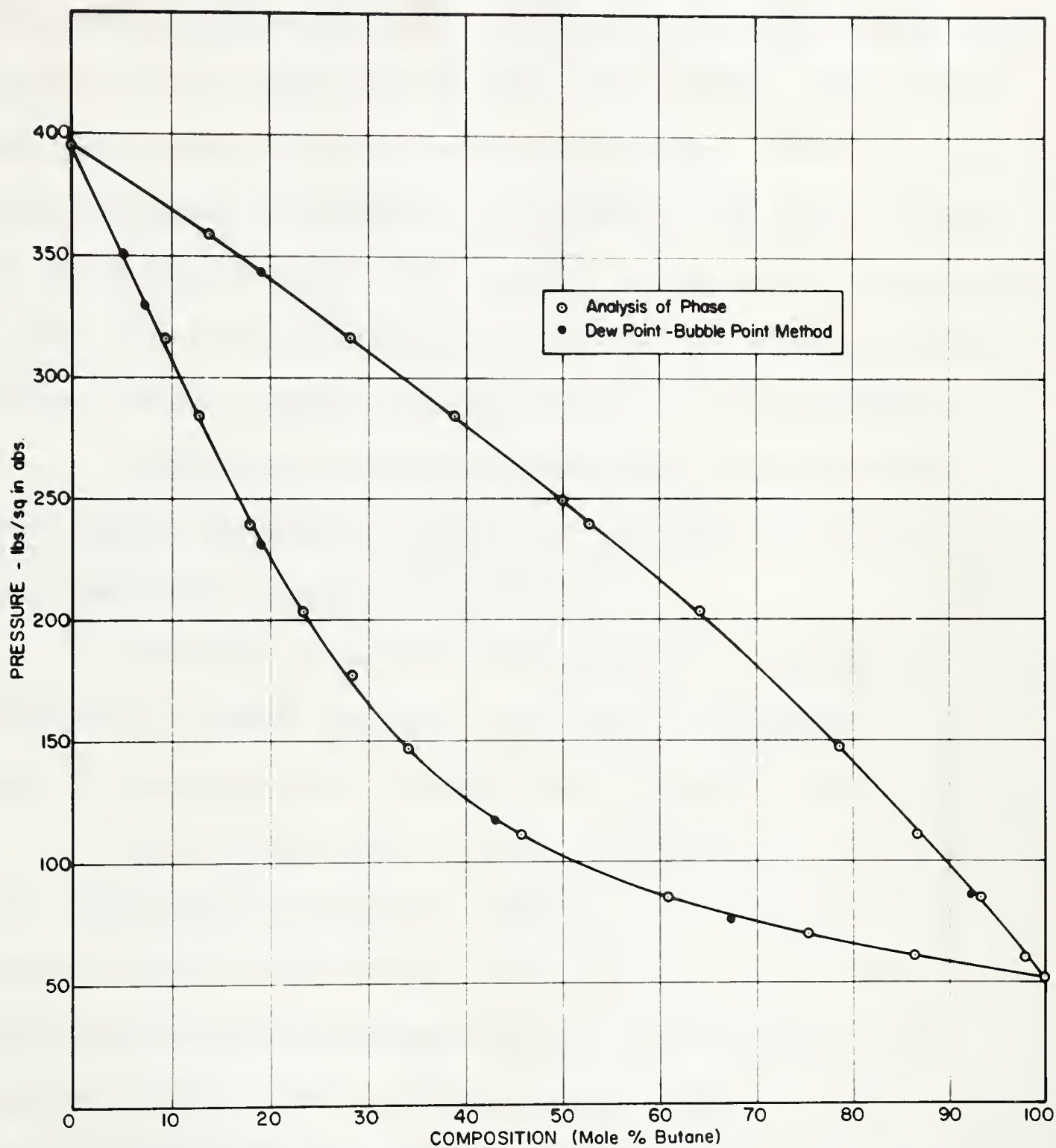


FIG. 22. PRESSURE-COMPOSITION DIAGRAM AT 100°F OF THE SYSTEM n-BUTANE-HYDROGEN SULPHIDE

The points obtained by the dew point method were taken by observing condensation of the first drop of liquid on the glass window during compression of the gaseous sample. The points obtained using the bubble point method are the result of plotting the change of volume versus pressure, the marked change in slope indicating the bubble point. This method is illustrated by the data plotted in Figure 24 showing the bubble point obtained for the hydrogen sulphide used in these experiments.

Equilibrium ratios were calculated for n-butane and for hydrogen sulphide at 100°F, and are shown in Figure 23 and tabulated in Table 4 of Appendix I.

Volumetric data for three mixtures of hydrogen sulphide with n-butane are shown in Table 5 of Appendix I. Data are for pressures below the dew point pressure of each mixture.

The initial volume of each sample mixture was measured at a relatively low pressure; however, at this pressure the compressibility factor could not be taken as one. Therefore, the pressure-volume measurements were extrapolated to zero pressure using a power series expansion similar to that employed in the virial equation of state. The method of least squares was used to fit the data with an equation of the form

$$P = A + \left(\frac{1}{V} \right) B + \left(\frac{1}{V} \right)^2 C \quad \text{when } A \rightarrow 0$$

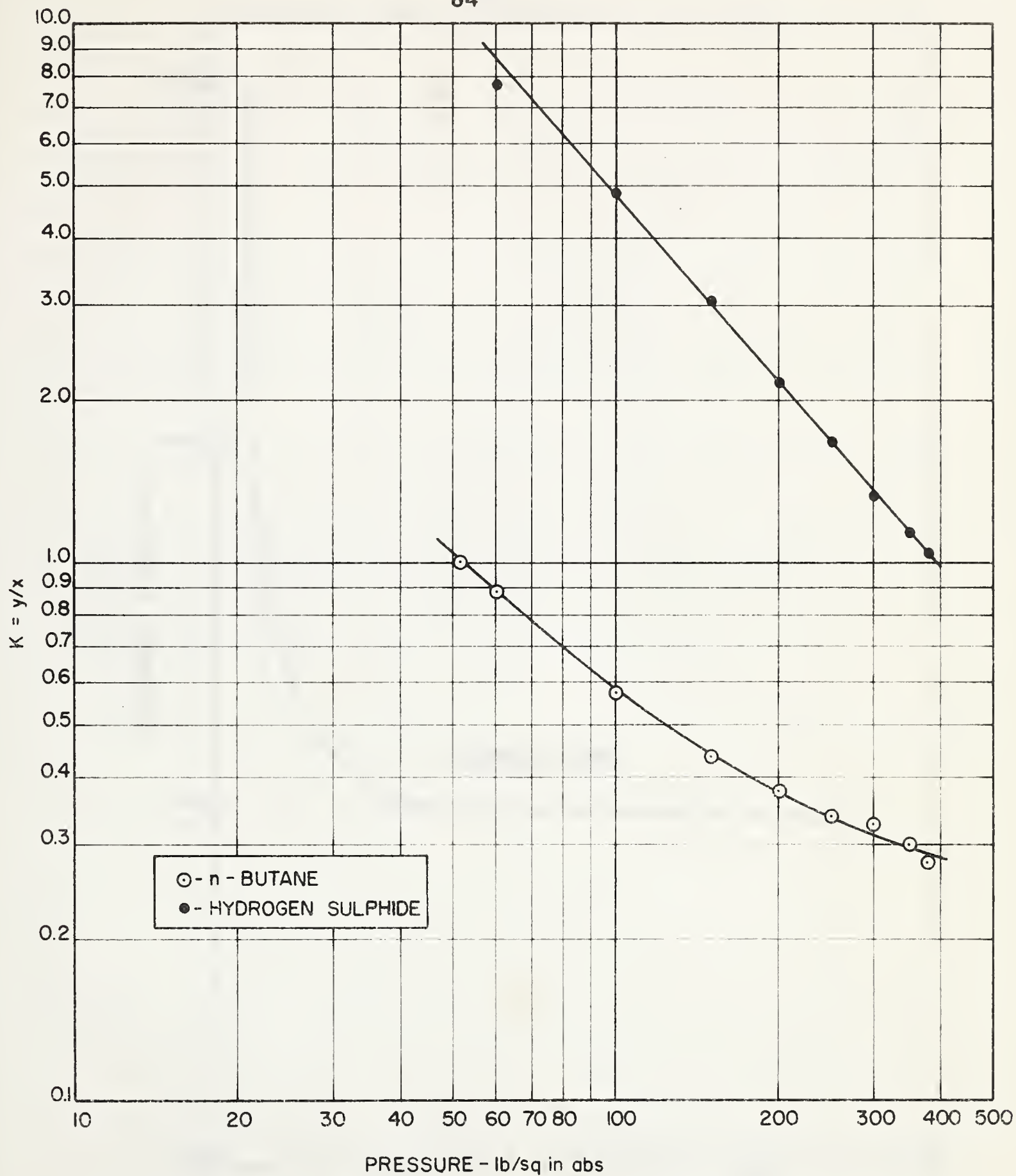


FIG. 23. EQUILIBRIUM RATIOS FOR THE SYSTEM n-BUTANE - HYDROGEN SULPHIDE AT 100°F

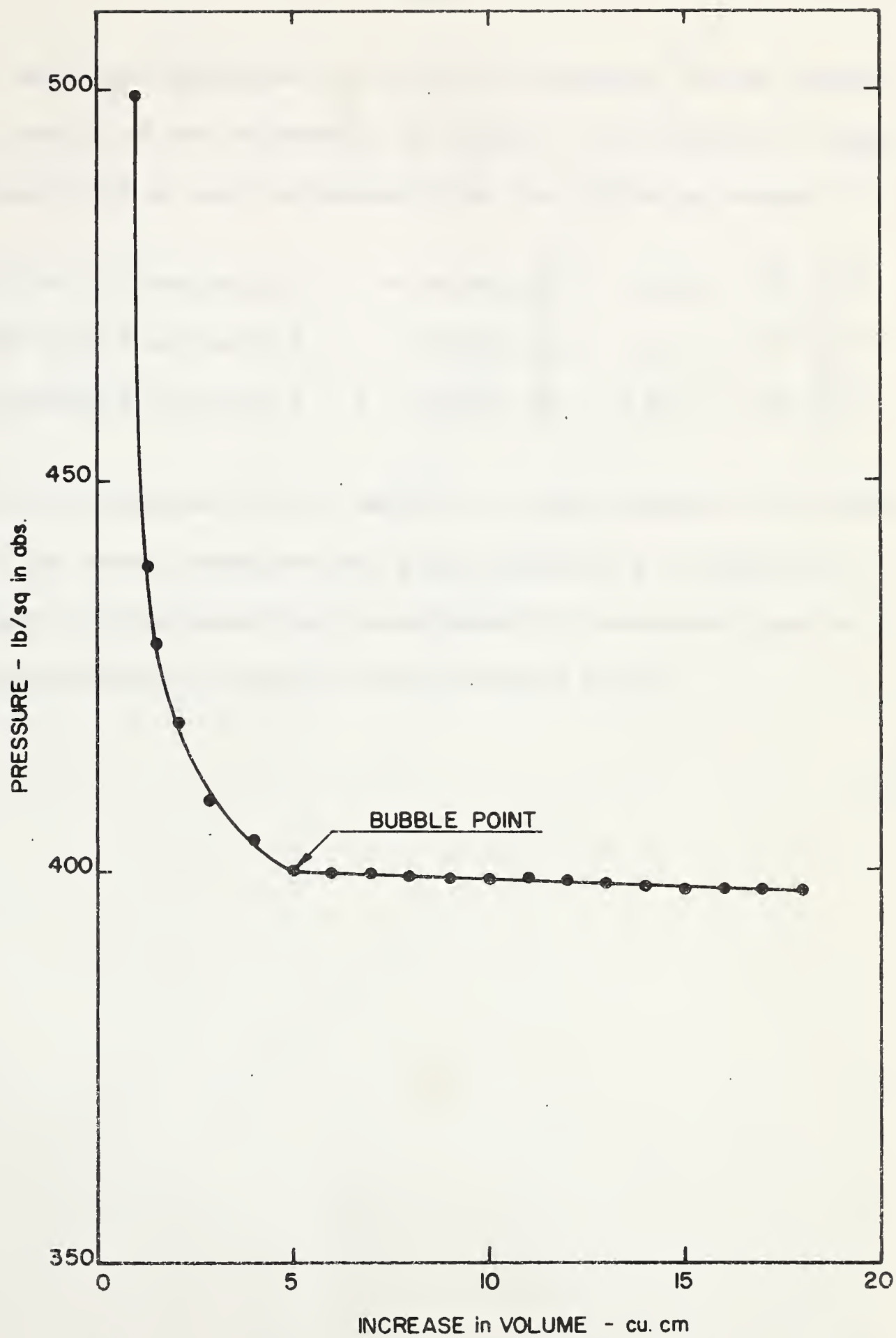


FIG. 24. DIAGRAM OF HYDROGEN SULPHIDE BUBBLE POINT

The data were processed on the LGP 30 computer at the Computing Centre of the University of Alberta. The number of moles of each mixture was calculated from the following curves

$$\begin{array}{ll}
 0.564 \text{ mole fraction H}_2\text{S} & P = 54,908 \left(\frac{1}{V}\right) - 2.966 \times 10^6 \left(\frac{1}{V}\right)^2 \\
 0.805 \text{ mole fraction H}_2\text{S} & P = 30,810 \left(\frac{1}{V}\right) - 6.197 \times 10^5 \left(\frac{1}{V}\right)^2 \\
 0.945 \text{ mole fraction H}_2\text{S} & P = 44,100 \left(\frac{1}{V}\right) - 0.951 \times 10^6 \left(\frac{1}{V}\right)^2
 \end{array}$$

Values of compressibility factors at even pressures calculated from the above equations are given in Table 6 of Appendix I. Figure 25 illustrates the experimentally determined compressibility factors along with the smoothed curves.

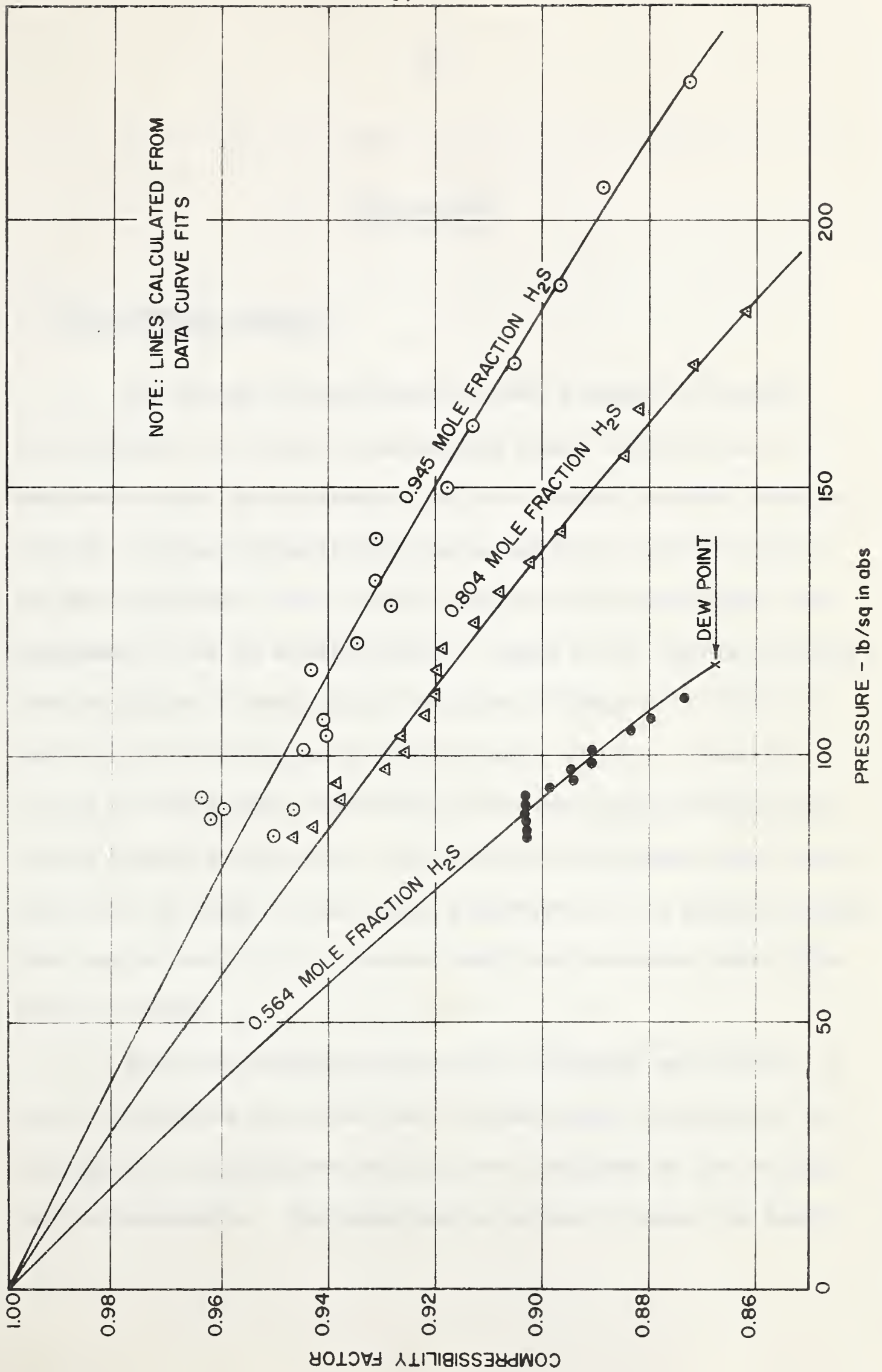


FIG. 25. COMPRESSIBILITY FACTORS FOR n-BUTANE - HYDROGEN SULPHIDE MIXTURES AT 100°F

F DISCUSSION

1 EXPERIMENTAL RESULTS

The system n-butane-methane was studied to examine the methods to be used in performing phase equilibrium experiments with the equipment, and to compare the data obtained to that of other investigators as a check on the reliability of the techniques. The results indicated the procedures and equipment to be in working order. Rigas et al (55) attributed the deviation of their data from that of Sage et al (60) to small amounts of ethane in their charge samples. However, it may be noted that the present work and that of Rigas agree in the liquid region while the present work agrees more closely with that of Sage at the higher pressures in the gaseous region. The samples used in the present work were somewhat purer than those of Rigas.

From the compressibility data obtained on methane, it can be concluded that over the limited range of pressures investigated, satisfactory accuracy was obtained in the volumetric measurements. The experiments served to show the feasi-

bility of obtaining volumetric data with the equipment rather than to confirm the overall calibrations.

Figure 26 shows the phase equilibria data for the system hydrogen sulphide - n-butane in comparison with that of the propane-hydrogen sulphide system (29) and the hydrogen sulphide - n-pentane system (50). It will be noted that the n-butane binary system follows the general pattern of the n-pentane curves for dew and bubble points, with no indication of the azeotropic behavior found in the propane system. Good agreement exists between the data obtained of the n-butane system by the visual dew point method and the analysis technique. The volumetric bubble point technique also compared well with the analysis technique.

Although the pressures were rather low, volumetric measurements were made on some of the samples that were of a convenient volume prior to dew point measurements. A weighing bomb method or a volume measuring charge cell would eliminate the need for extrapolations of the data to determine the exact amount of material in the cell. Nevertheless, the results obtained by the latter method do not appear to be inconsistent. The compressibility factors calculated from the experimental data are within about ± 1 per cent of the com-

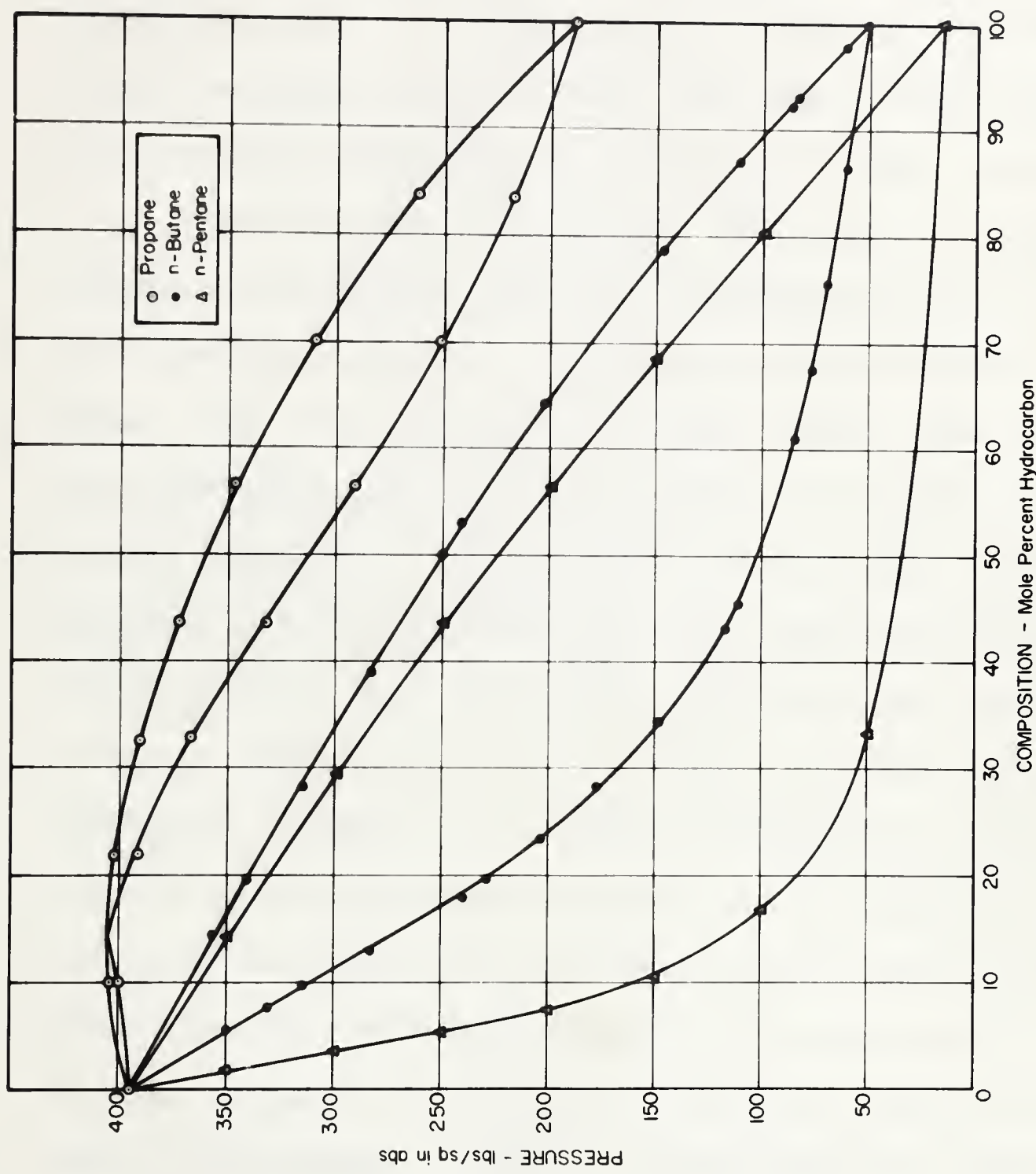


FIG. 26. PRESSURE - COMPOSITION DIAGRAMS AT 100°F OF THE SYSTEMS HYDROGEN SULPHIDE - PROPANE, HYDROGEN SULPHIDE - n-BUTANE AND HYDROGEN SULPHIDE - n-PENTANE

compressibility factors calculated from the smoothed curves.

Equilibrium ratios were calculated for n-butane by the following methods: the ideal solution K concept (24), the NGSMA convergence pressure method (36), and the Winn convergence pressure method using the nomogram of Hadden and Grayson (21). These are shown in Figure 27. Also shown are the experimental equilibrium ratios for the systems methane - n-butane (60), hydrogen sulphide - n-butane, and carbon dioxide - n-butane (40). The experimental K values for the three systems are essentially the same up to a pressure of 100 psia, but deviate thereafter. The predicted values are also in better agreement at pressures below 100 psia. The ideal solution K values are lower than the hydrogen sulphide binary experimental values by about 30 per cent at 350 psia. The ideal solution prediction is better for the other two experimental systems, the deviation being minus 10 per cent for the methane system and minus 15 per cent for the carbon dioxide system. The NGSMA predictions and the Winn predictions were calculated for the hydrogen sulphide - n-butane system, and as a result, do not apply to the methane - n-butane system because the convergence pressures of the two systems are not the same. It should be noted that in dealing with the convergence pressure methods,

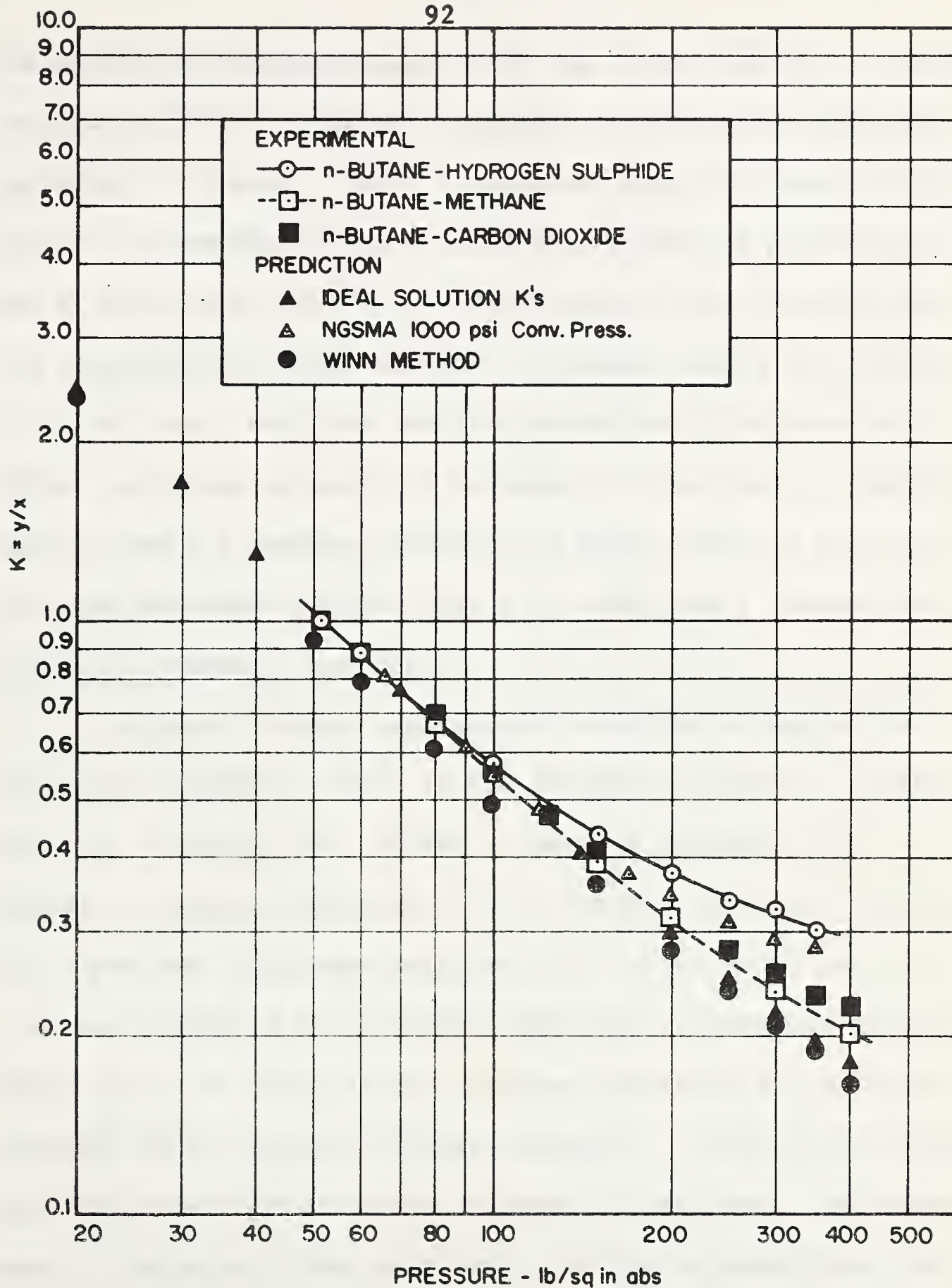


FIG. 27. EQUILIBRIUM RATIOS FOR n-BUTANE AT 100°F

the operating temperature of 100°F was lower than the critical temperature of the lightest component in the system hydrogen sulphide - n-butane. Thus, a quasi-convergence pressure was used as recommended by each particular method of prediction. The K values predicted by the NGSMA method were greater than the experimental carbon dioxide - n-butane values by a maximum of 20 per cent, and less than the experimental hydrogen sulphide - n-butane values by a maximum of 10 per cent. The Winn method showed a maximum deviation of about minus 30 per cent from the hydrogen sulphide system K values and a minimum deviation of minus 10 per cent.

Figure 28 shows experimental equilibrium ratios for hydrogen sulphide at 100°F in the following systems: methane - hydrogen sulphide (49), ethane - hydrogen sulphide (27), propane - hydrogen sulphide (29), n-butane - hydrogen sulphide, and n-pentane - hydrogen sulphide (53). Also shown are the K values predicted by the NGSMA 1000 psia convergence pressure chart (36). At 390 psia the K values predicted for hydrogen sulphide in the system hydrogen sulphide - n-butane are higher than the experimental values by about 25 per cent. The agreement is better at lower pressures. Of the systems shown, the propane - hydrogen sulphide K values deviate the greatest

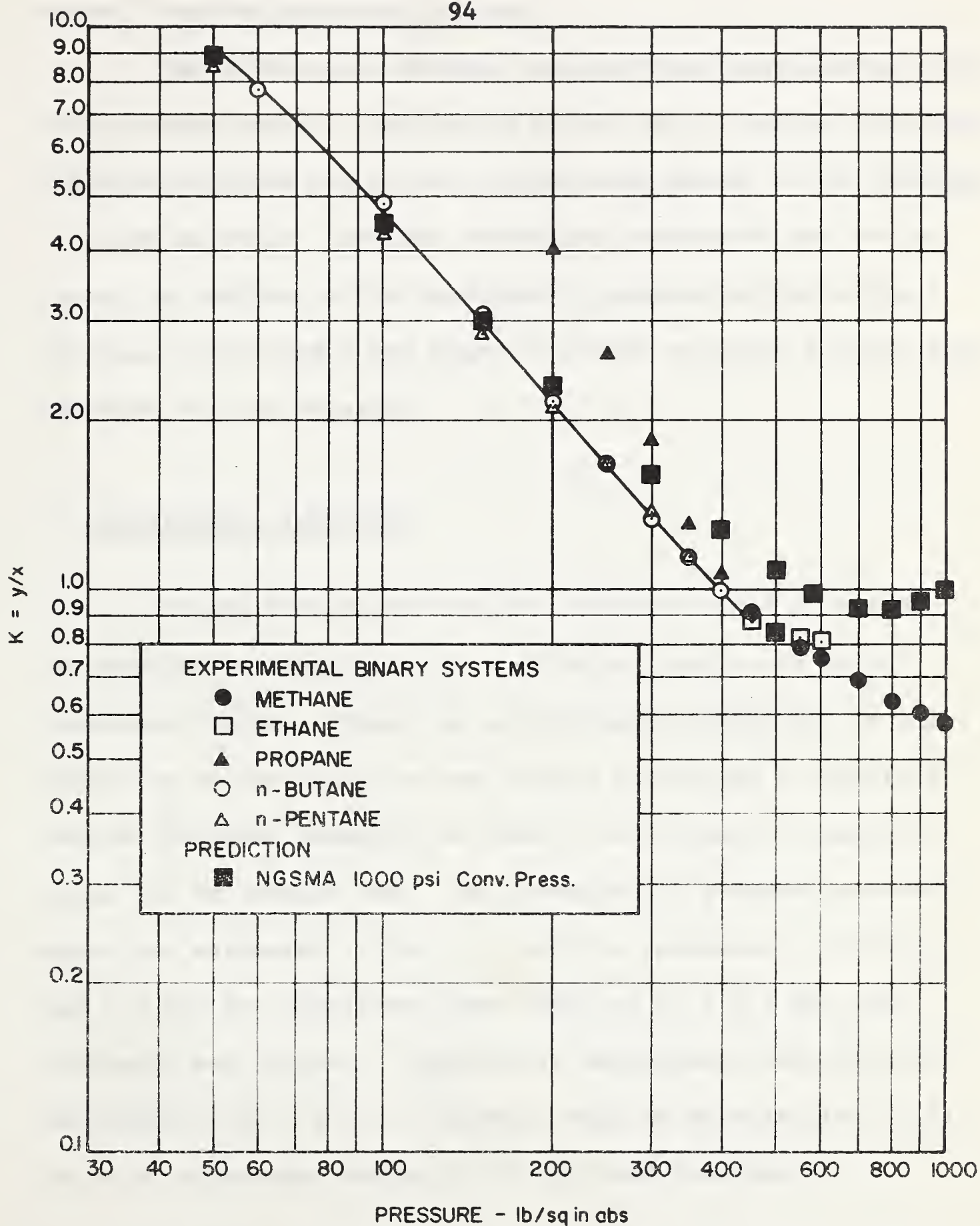


FIG. 28. EQUILIBRIUM RATIOS FOR HYDROGEN SULPHIDE
AT 100°F

amount from the predicted values.

The differences between the predicted equilibrium ratios and the experimental equilibrium ratios in the system containing hydrogen sulphide may be due to the polar nature of the hydrogen sulphide molecule. Systems containing azeotropes are not expected to conform to the convergence pressure method of prediction. The propane and ethane hydrogen sulphide systems were examples of this behavior.

2 EXPERIMENTAL EQUIPMENT

It has been shown that the equipment will be useful in carrying out vapor-liquid equilibrium studies in multi-component systems. There is considerable flexibility in the operation of the cell; dew and bubble points may be obtained, samples of either phase may be taken, and volumetric measurements may be carried out. The precision of pressure measurements was estimated to be ± 0.5 psi for pressures to 1000 psi and ± 5 psi for pressures above 1000 psi or ± 0.2 per cent, whichever was largest. Temperature measurement precision was estimated to be $\pm 0.1^\circ\text{C}$. Volumes could be measured to ± 0.01 cu cm or a probable error of ± 0.001 mole fraction.

The double-acting pump and piston combination has performed satisfactorily with the exception of the neoprene "O" ring on the piston. The ring hardened in the presence of hydrogen sulphide. Further testing will probably be necessary in order to reach maximum design pressures in the cell. As assembled at present, a leak in the cell window gasket may be anticipated before a pressure of 5000 psi is reached, judging only from the previous experiments with teflon gaskets.

When operating in regions near the critical pressure and temperature of the system, the densities of the liquid phase and gas phase are very close, and as a result the spraying of liquid only does not work too well. However, mercury, being much denser than either phase, may be sprayed instead. The spraying of mercury may also be used for mixtures in the single phase region, the resulting turbulence causing the mixing of the components. At the same time, the "jetting" of the hydrocarbons through the small internal "valve" port provides good mixing. When the phases are very close in densities, more time is likely to be required to obtain the necessary equilibrium conditions.

G CONCLUSIONS

1. New equipment for the study of vapor-liquid equilibrium was built and shown to be useful by experiments on the system n-butane-methane at 100°F.
2. The pressure-composition diagram of the system hydrogen sulphide-n-butane was determined at 100°F.
3. It was shown that no azeotrope exists in the hydrogen sulphide-n-butane system at 100°F.
4. The predicted K values and the experimental K values for the components in the hydrogen sulphide-n-butane system were in agreement to pressures of 100 psia. Deviations up to about 30 per cent could be encountered for pressures to 350 psia.

NOMENCLATURE

C	=	number of components
F	=	number of degrees of freedom
f_l	=	fugacity in the liquid phase
f_g	=	fugacity in the gas phase
K	=	equilibrium ratio
k	=	external radius divided by internal radius (r_2/r_1)
m	=	Poisson ratio
N	=	number of phases
n	=	number of moles
P	=	pressure
P_1	=	internal pressure
P_2	=	external pressure
P_b	=	bursting pressure
P_v	=	vapor pressure
R	=	gas constant
r	=	radius
r_1	=	internal radius
r_2	=	external radius
s	=	safety factor
T	=	temperature

- V - volume
- x_i - mole fraction in the liquid phase
- y_i - mole fraction in the gas phase
- Z - compressibility factor
- a - axial stress
- e - tensile stress at the elastic limit
- r - radial stress
- s - shear stress
- t - tangential or hoop stress
- v - ultimate tensile stress
- y - yield stress

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A P P E N D I X I

TABLE 1

VAPOR-LIQUID EQUILIBRIUM DATA FOR
THE SYSTEM N-BUTANE-METHANE AT 100°F

Pressure lb/sq in abs	Composition Gas		— weight fraction Liquid	
	CH ₄	nC ₄ H ₁₀	CH ₄	nC ₄ H ₁₀
111	0.2065	0.7935		
162			0.0137	0.9863
			0.0120	0.9880
175	0.3478	0.6522		
180	0.3665	0.6335	0.0137	0.9863
840	0.6637	0.3363	0.0911	0.9089
1054	0.6597	0.3403	0.1270	0.8730
1080	0.6847	0.3153		
1153	0.6738	0.3262	0.1465	0.8535
	0.6707	0.3293	0.1433	0.8567
1304	0.6687	0.3313	0.1729	0.8271
			0.1710	0.8290
1430	0.6456	0.3544		
	0.6495	0.3505		
1452	0.6515	0.3485	0.2006	0.7994
1524	0.6365	0.3635	0.2290	0.7710
1539	0.6243	0.3757	0.2304	0.7696

TABLE 2

METHANE COMPRESSIBILITY FACTORS

Pressure lb/sq in abs	Compressibility Factor	
	This work	Olds et al (60)
730	0.922	0.923
628	0.932	0.934
528	0.943	0.944
397	0.954	0.957
336	0.960	0.963

TABLE 3

VAPOR-LIQUID EQUILIBRIUM DATA FOR THE
SYSTEM N-BUTANE-HYDROGEN SULPHIDE AT 100°F

Pressure lb/sq in abs	Composition gas		— mole fraction liquid	
	H ₂ S	nC ₄ H ₁₀	H ₂ S	nC ₄ H ₁₀
60.4	0.133	0.867	0.021	0.979
69.4	0.243	0.757		
75.3	0.322	0.678		
84.8	0.386	0.614	0.066	0.934
88.0			0.076	0.924
111.0	0.539	0.461	0.131	0.869
117.0	0.564	0.436		
146.8	0.655	0.345	0.209	0.791
176.6	0.713	0.287		
203.4	0.763	0.237	0.355	0.645
230.4	0.805	0.195		
239.3	0.818	0.182	0.468	0.532
249.0			0.497	0.503
283.8	0.870	0.130	0.607	0.393
315.8	0.904	0.096	0.716	0.284
329.8	0.924	0.076		
343.0			0.805	0.195
350.7	0.945	0.055		
358.8			0.858	0.142

TABLE 4

EQUILIBRIUM RATIOS FOR THE SYSTEM
N-BUTANE-HYDROGEN SULPHIDE AT 100°F

Pressure lb/sq in abs	Equilibrium Ratios	
	H ₂ S	nC ₄ H ₁₀
51.6	-----	1.000
60.0	7.660	0.882
100.0	4.840	0.573
150.0	3.037	0.437
200.0	2.160	0.375
250.0	1.667	0.339
300.0	1.339	0.328
350.0	1.143	0.300
380.0	1.043	0.277
394.0	1.000	-----

TABLE 5

PRESSURE VOLUME DATA FOR THE
SYSTEM N-BUTANE-HYDROGEN SULPHIDE AT 100°F

MOLE FRACTION H₂S

<u>0.564</u>		<u>0.804</u>		<u>0.945</u>	
Pressure lb/sq in abs	$\frac{1}{\text{volume}} \text{ (cm)}^{-3}$	Pressure lb/sq in abs	$\frac{1}{\text{volume}} \text{ (cm)}^{-3}$	Pressure lb/sq in abs	$\frac{1}{\text{volume}} \text{ (cm)}^{-3}$
84.8	0.00171	84.8	0.00291	85.2	0.00203
86.3	0.00174	86.8	0.00299	88.7	0.00209
87.8	0.00177	91.8	0.00318	90.2	0.00213
89.3	0.00180	94.8	0.00328	92.7	0.00218
90.8	0.00183	97.3	0.00340	94.7	0.00228
92.8	0.00187	100.3	0.00352	101.7	0.00244
93.8	0.00190	103.8	0.00364	103.7	0.00250
95.3	0.00194	107.3	0.00378	106.7	0.00257
97.3	0.00198	111.3	0.00393	115.7	0.00278
98.8	0.00202	115.8	0.00409	121.2	0.00294
100.8	0.00206	120.8	0.00427	128.2	0.00313
104.8	0.00216	125.3	0.00446	132.7	0.00323
106.8	0.00221	130.3	0.00466	141.7	0.00345
110.8	0.00231	135.8	0.00489	150.2	0.00371
		141.8	0.00514	161.2	0.00400
		155.8	0.00572	173.7	0.00435
		164.8	0.00607	188.2	0.00476
		173.3	0.00646	206.2	0.00526
		183.3	0.00691	226.2	0.00588

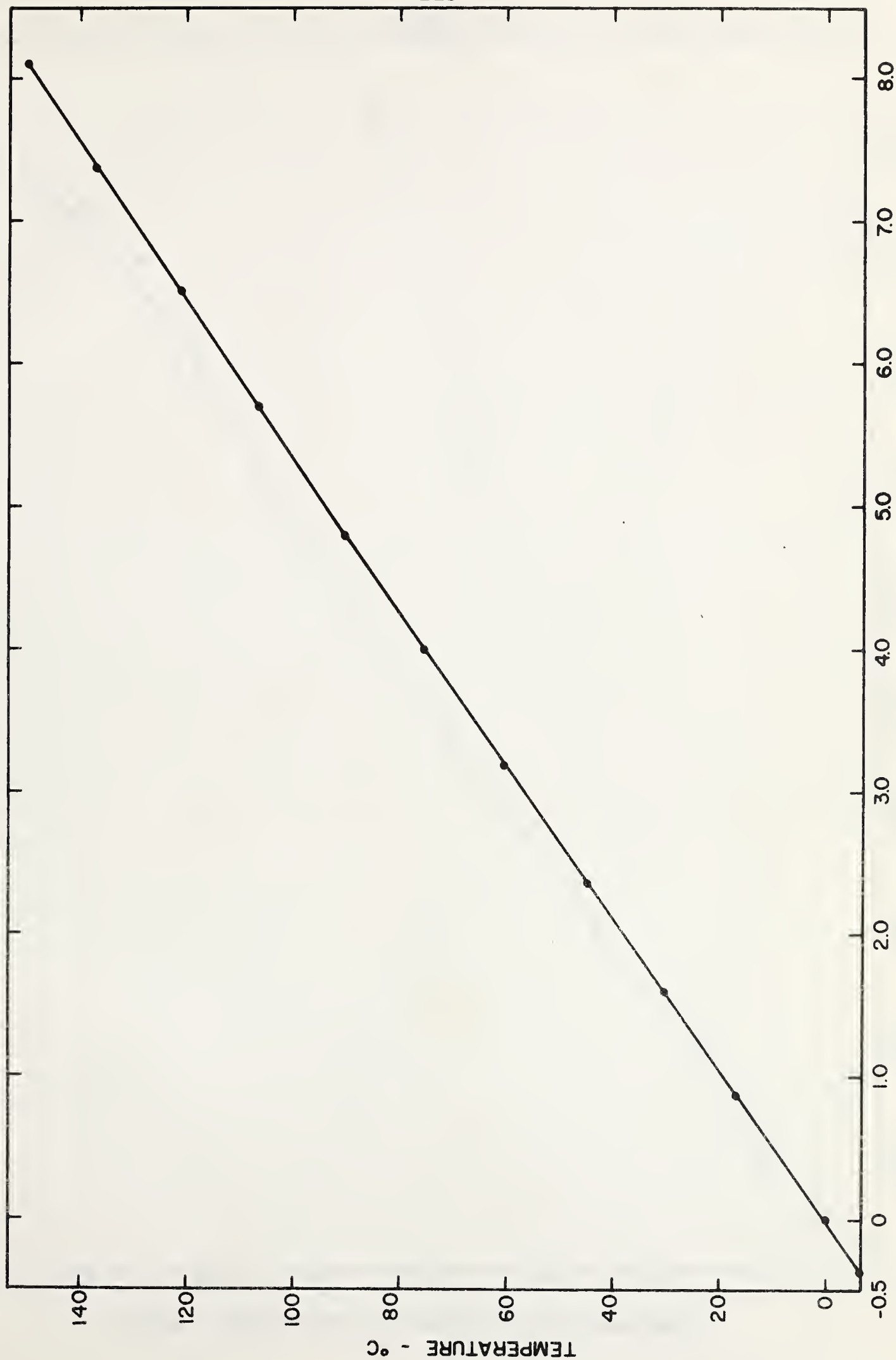
TABLE 6

SMOOTHED COMPRESSIBILITY FACTORS FOR THE
SYSTEM N-BUTANE-HYDROGEN SULPHIDE AT 100°F

Pressure Lb/sq in abs	Mole Fraction H ₂ S		
	0.955	0.805	0.564
14.7	0.9925	0.9905	0.9850
20	0.9900	0.9871	0.9798
30	0.9850	0.9803	0.9692
40	0.9800	0.9732	0.9587
50	0.9749	0.9660	0.9478
75	0.9620	0.9480	0.9200
100	0.9483	0.9299	0.8896
125	0.9345	0.9104	
150	0.9201	0.8903	
200	0.8900	0.8460	

Note: the figures are significant to three places only

A P P E N D I X I I



ELECTROMOTIVE FORCE - Millivolts

FIG. 29. IRON - CONSTANTAN THERMOCOUPLE CALIBRATION

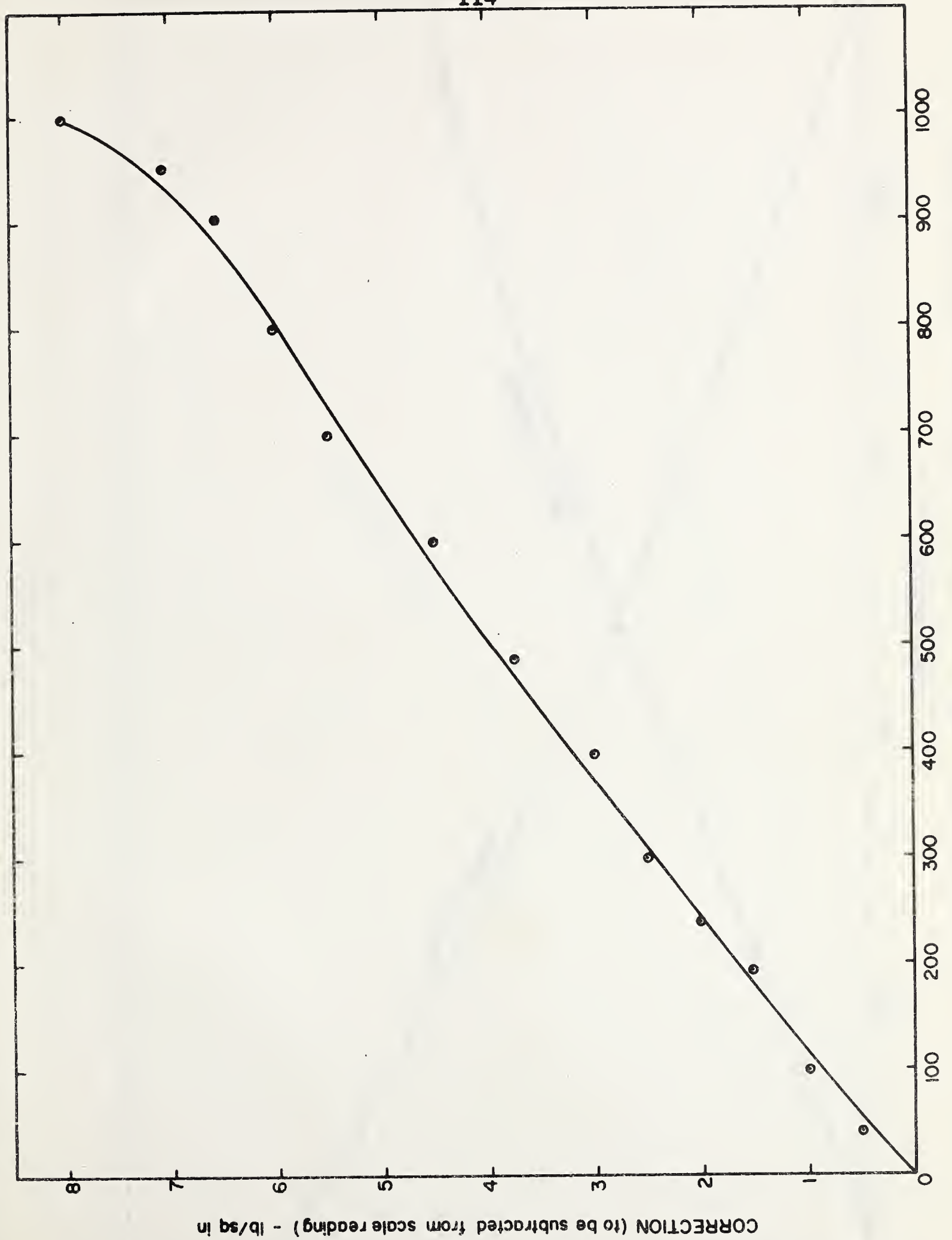


FIG. 30. CALIBRATION OF HEISE GAUGE No H 8566

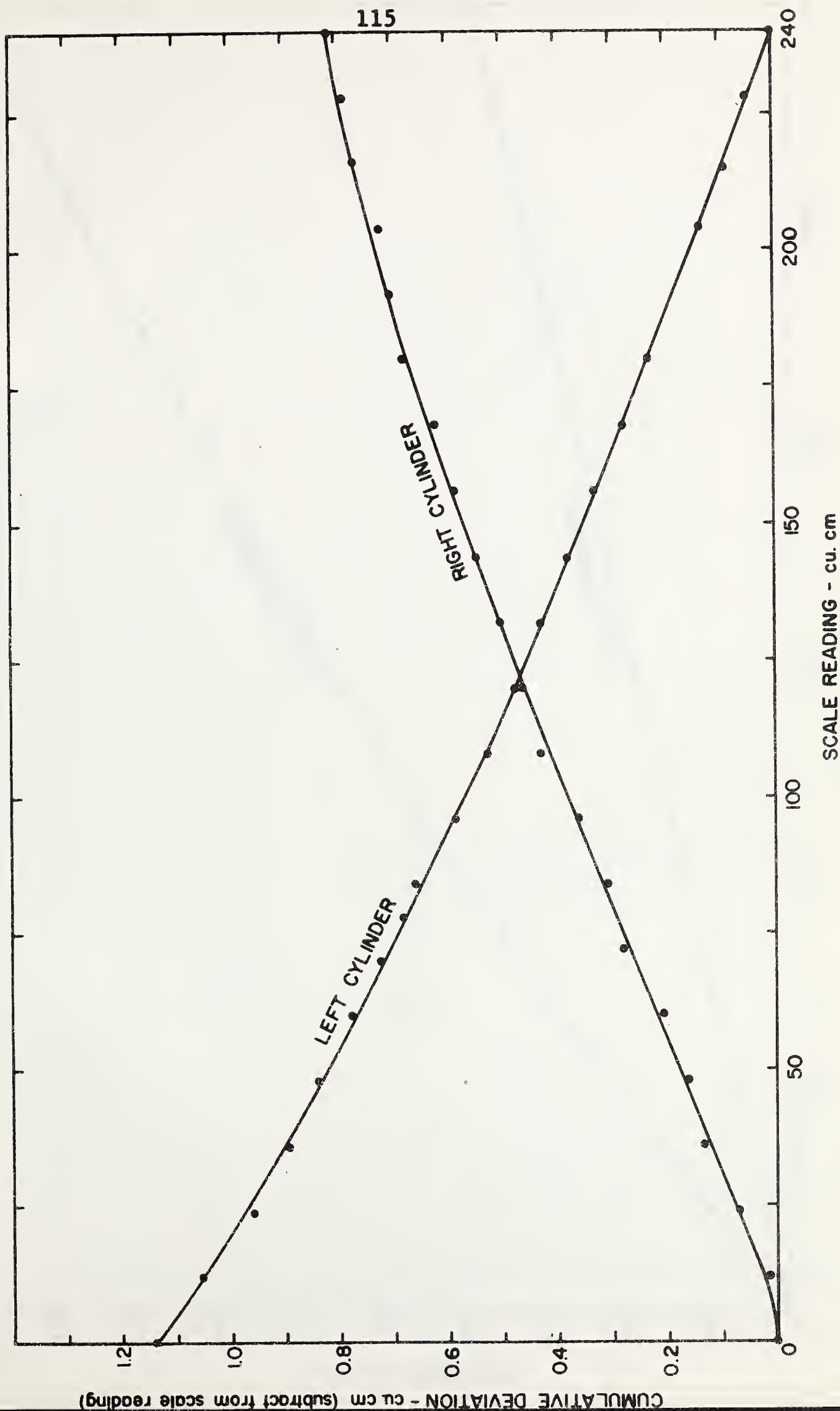


FIG. 31. VOLUMETRIC CALIBRATION OF DOUBLE-ACTING PUMP

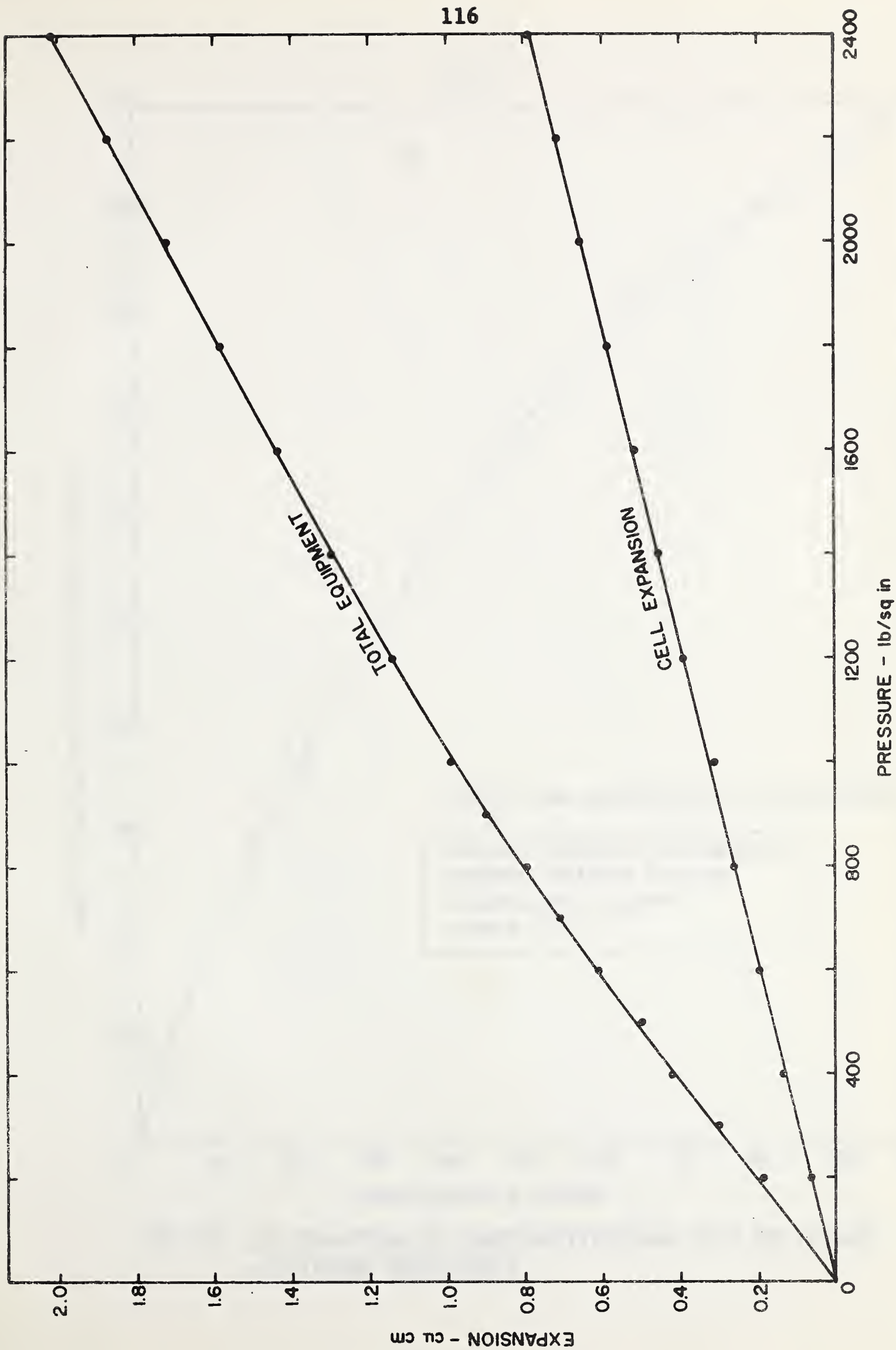


FIG. 32. VOLUMETRIC CALIBRATION FOR EFFECT OF PRESSURE ON CELL VOLUME

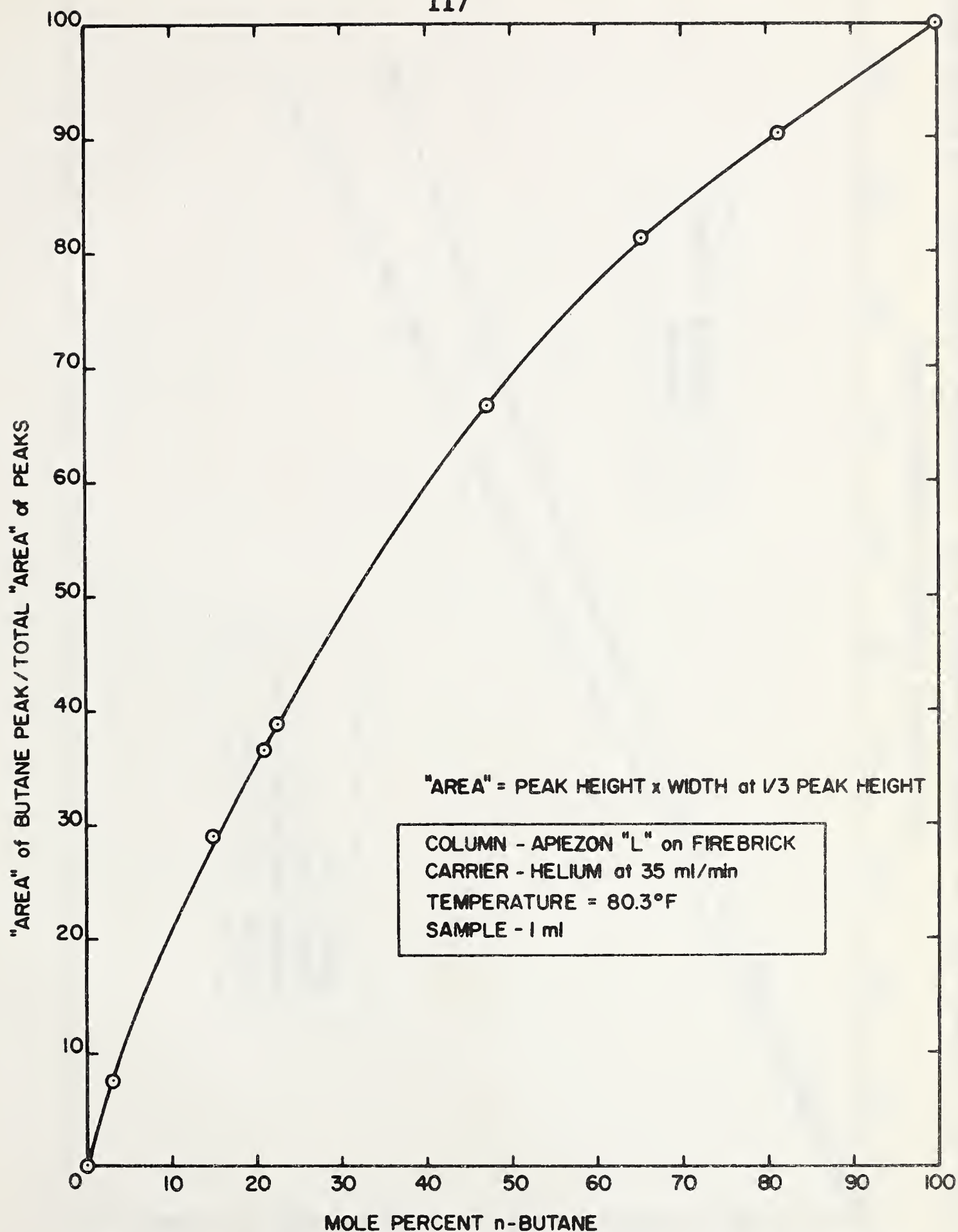


FIG. 33. CALIBRATION OF CHROMATOGRAPH FOR METHANE-n-BUTANE MIXTURES

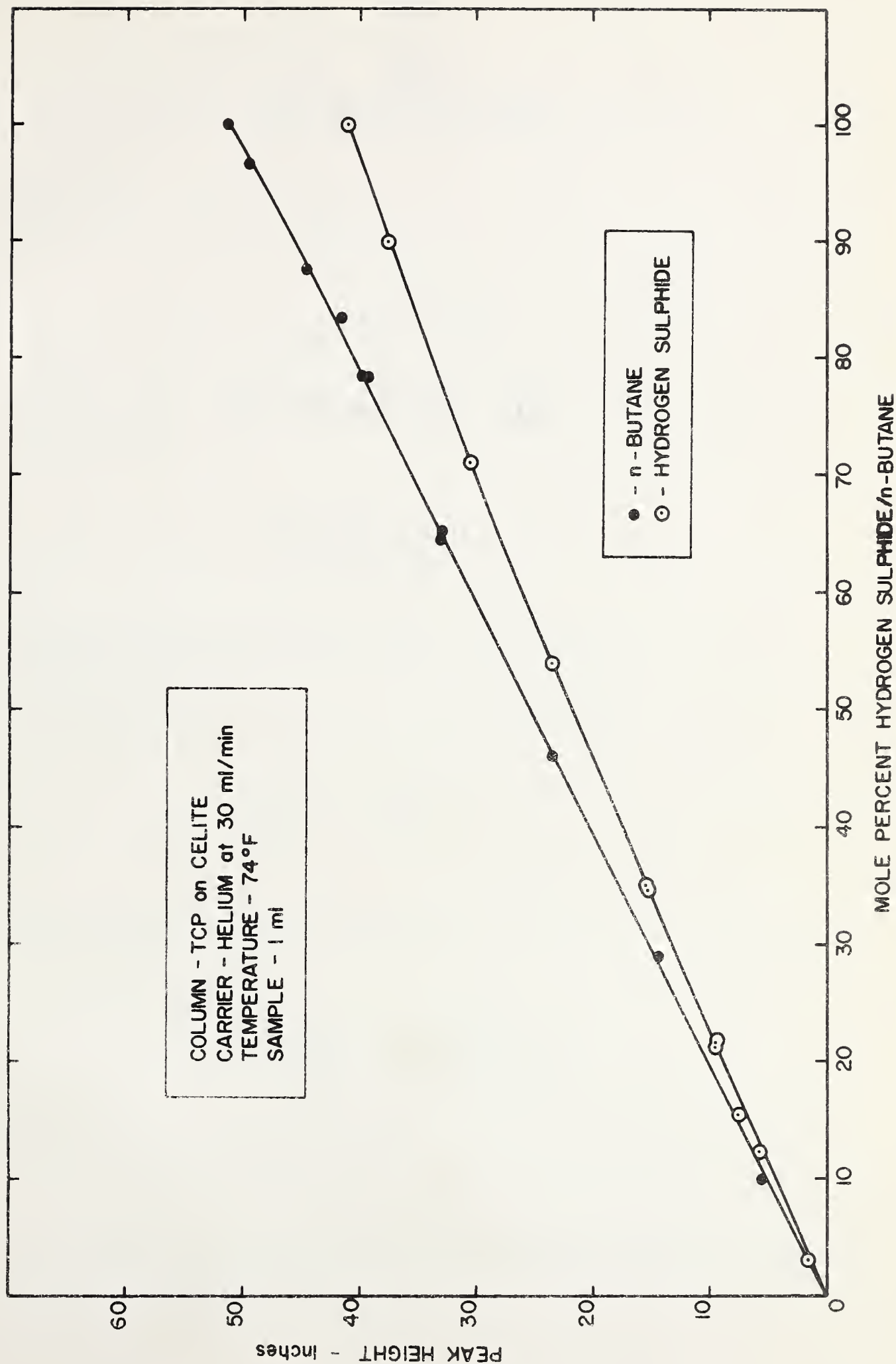


FIG. 34. CALIBRATION OF CHROMATOGRAPH FOR n-BUTANE-HYDROGEN SULPHIDE MIXTURES

A P P E N D I X I I I



SAMPLE CALCULATIONS1. CELL WALL SAFETY FACTOR

$$k = \sqrt{\frac{\sigma_y}{\sigma_y - s P \sqrt{3}}}$$

rearranging

$$s = \frac{\sigma_y (k^2 - 1)}{P (k^2 \sqrt{3})}$$

for 316 stainless steel $\sigma_y = 40,000$ psi

design pressure, $P = 8,000$ psi

$$k = \frac{r_2}{r_1} = \frac{5.375}{2.375} = 2.26$$

substituting in above equation

$$s = \frac{40,000}{8,000} \frac{(2.26)^2 - 1}{(2.26)^2 1.732}$$

$$s = 2.3$$

therefore, the safety factor for the cell wall at minimum thickness was 2.3

2. DOUBLE ACTING PUMP CYLINDER WALL SAFETY FACTOR

$$s = \frac{\sigma_y (k^2 - 1)}{P (k^2 \sqrt{3})}$$

for 416 stainless steel $\sigma_y = 45,000$ psi

design pressure, $P = 8,000$ psi

$$k = \frac{r_2}{r_1} = \frac{2.688}{1.375} = 1.955$$

substituting in above equation

$$s = \frac{45,000}{8,000} \frac{(1.955)^2 - 1}{(1.955)^2 1.732}$$

$$s = 2.4$$

therefore, the safety factor for the cylinder wall was 2.4

TABLE 7

EQUIPMENT CLASSIFICATIONS

Class	Reference Number
1. Static, Variable Volume	- 62, 23, 70, 73, 9, 33, 25, 14, 57, 15, 12, 69, 13, 55, 74.
2. Static, Isochoric	- 68, 5, 32, 6.
3. Bubble Point-Dew Point	- 29, 20, 38, 11.
4. Recirculation	- 1, 43.
5. Dynamic Flow	- 76, 35.
6. Equilibrium Still	- 66, 3.
7. Windowed	- 33, 25, 14, 57, 15, 12, 69, 6, 29, 20, 38, 11, 43, 66.
8. Mechanical Agitator	- 62, 23, 9, 69, 55, 68, 32, 6, 29, 20, 38, 11.
9. Agitation by Rocking	- 70, 73, 33, 25, 14, 57, 15, 12, 13, 74, 5.
10. Piston in cell	- 12, 69, 13, 55.
11. Volumetric Measurements	- 62, 33, 25, 14, 57, 15, 12, 13, 74, 68, 6, 29, 20, 38, 11.

Note: The reference numbers are listed in the order that they appear in the report.

